Corrosion

THIS MONTH'S COVER—Marked corrosion is shown along the Luders (strain) lines of these steel reclaimer reboiler tubes. The bundle from which they were taken was in a water-amine gas treating unit removing carbon dioxide. This damage took place in 18 months at approximately 165 to 190 F.

☆

CONTENTS

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THE NATIONAL ASSOCIATION OF CORROSION ENGINEERS

is a non-profit, scientific and research association of individuals and companies concerned with corrosion or interested in it, whose objects are:

(a) To promote the prevention of corrosion, thereby curtailing economic waste and conserving natural resources.

(b) To provide forums and media through which experiences with corrosion and its prevention may be reported, discussed and published for the common good.

(c) To encourage special study and research to determine the fundamental causes of corrosion, and to develop new or improved techniques for its prevention.

(d) To correlate study and research on corrosion problems among technical associations to reduce duplication and increase efficiency.

(e) To promote standardization of terminology, techniques, equipment and design in corrosion control.

(f) To contribute to industrial and public safety by promoting the prevention of corrosion as a cause of accidents.

(g) To foster cooperation between individual operators of metallic plant and structures in the joint solution of common corrosion problems.

(h) To invite a wide diversity of memberships, thereby insuring reciprocal benefits between industries and governmental groups as well as between individuals and corporations.

It is an incorporated association without capital stock, chartered under the laws of Texas. Its affairs are governed by a Board of Directors, elected by the general membership. Officers and elected directors are nominated by a nominating committee in accordance with the articles of organization. Election is by the membership.

Inquiries regarding membership, and all general correspondence should be directed to the Executive Secretary at the administrative headquarters of the National Association of Corrosion Engineers at 1061 M & M Building, No. 1 Main Street, Houston 2, Texas.

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Topic of the Month

A Method of Protecting Pipe Type Cables

By F. E. KULMAN*

DURING the past 10 years, several hundred miles of pipe type cable have been installed in urban areas to transmit electric energy at high voltage, usually 69 or 138 kilovolts. Figure 1 shows a view of three paper insulated cables in a 6-inch steel pipe. The pipe is coated with asphalt mastic for corrosion protection.

In order to provide fault current protection, the sections of pipe are welded together and the pipe is grounded to the station ground bus at both terminations.

For cathodic protection of the pipe, it is necessary to lower the potential of the pipe so that it becomes negative by a small voltage to the earth, station ground bus, water pipes and other grounded structures. This double requirement of grounding and maintaining a negative pipe potential has been met in the past by installing a large 2-volt lead acid storage cell in the grounding connection between the pipe and the station ground bus. This resulted in good grounding and in addition provided cathodic protection. However, the batteries required periodic inspection and maintenance.

Unforeseen difficulties arose from unwanted stray railway currents which flowed between the ground buses via the pipe, charging the battery on one end of the line and discharging the battery at the other end. Occasionally when an accidental contact developed between the cable pipe and bare cast iron or steel mains in the congested streets, the batteries became short-circuited. Furthermore, the 2-volt potential was more than enough for corrosion protection.

Resistor and Rectifier Used

In 1954, a method of cathodic protection was developed which overcomes these difficulties. In this method, a 0.004-ohm resistor capable of carrying the cable fault current is connected between the pipe and station ground.

* Consolidated Edison Company of New York, Inc.

The resistor consists of two stainless steel bars connected in parallel, each bar 12 feet long and $\frac{1}{4}$ x 2 inches in section. The bars are formed into the shape of a "W" for compactness. A 100-ampere rectifier is connected across the resistor in such a way as to maintain the pipe end at 0.4 volt negative potential with respect to the station ground. This arrangement requires very little maintenance and is cheaper than the method which employs the batteries. Furthermore the potential applied to the pipe can be adjusted by selecting the rectifier current.

Figure 2 shows the application of the method to two 138-kilovolt feeders at an oil pump house in New York. The rectifier may be seen mounted on the wall with the resistor mounted under it. On the right may
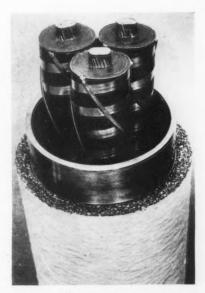
Figure 1—Three paper insulated cables in a 6-inch steel pipe.

Figure 2—Cathodic protection rectifier and resistor.
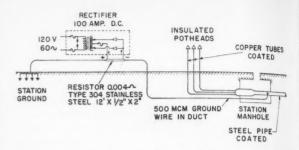
Figure 3—Schematic drawing of electrical circuit in which 0.4 volt output from rectifier is used for cathodic protection.

be seen two 500 Mcm grounding cables, one from each of the underground pipes, connected to a copper bus which in turn is connected to the negative terminal of the rectifier and the resistor. On the left, the positive terminal of the rectifier and the resistor are seen connected to the station grounding bus. Figure 3 is a schematic drawing of the electrical circuit.

Experience with the resistor method has been satisfactory and its use is being extended as new pipe cables are installed on the Consolidated Edison Company System.

TECHNICAL PAPERS ON CORROSION WELCOMED

Authors of technical papers on corrosion are invited to submit them for review without invitation to the Editor of Corrosion. Write for "Guide for the Preparation and Presentation of Papers" sent free on request to prospective authors.

Control of Couples
Developed in Water Systems[*]

By G. B. HATCH

Introduction

CORROSION control in water systems often is complicated by the presence of dissimilar metals. The more obvious couples formed by the junctions of dissimilar metal components of the system are not too troublesome because the resultant galvanic attack can be controlled rather simply by conventional water treatment.[1,2] The couples which develop during operation of the system are more troublesome, though perhaps less obvious. Metal picked up from the more noble components deposits on the more anodic members and sets up galvanic cells. The cells which are formed in this manner are rather difficult to control with inhibitors.

Copper and many of its alloys such as brass, bronze, Admiralty, etc., are widely used in water systems and generally constitute the more noble components thereof. Water tends to pick up small amounts of copper while passing through cuprous portions of the system, the quantity picked being influenced by the length of time the water is in contact with the copper-bearing metals. Consequently, recirculating systems are more susceptible to trouble from dissolved copper than are once-through types. Copper pickup also is influenced markedly by the pH of the water and generally becomes appreciable in recirculating systems when the pH drops below 6.7 increasing progressively as the pH is lowered further.

Anodic components of a water system generally are iron or the low alloy steels. Copper dissolved from the cuprous portions of the system tends to deposit on these ferrous components and thus to set up galvanic cells.

Dissolved copper is detrimental to the protection of iron and steel with most inhibitors. It decreases inhibition and introduces or increases a tendency toward localization of attack and pitting. Consequently the pH in recirculating systems which involve copper and many of its alloys should be sufficiently high (6.7 or above) to prevent appreciable pickup of copper by the water if optimum protection of ferrous metals is to be attained. This limitation of pH imposed by the presence of cuprous metals greatly restricts the preferred range for protection of

G. B. HATCH—Head of corrosion research at Calgon, Inc., Pittsburgh, Pa. He received an AB and an AM degree from Oberlin College and a PhD from the University of Michigan; at the latter institution he specialized in colloid chemistry. Dr. Hatch has been associated with Calgon, Inc., since 1936.

Abstract

The presence of copper and its alloys in water systems complicates control of the corrosion of the ferrous metals present with inhibitors. The solution of copper by the water on passage through the cuprous portions of the system and its subsequent deposition on the ferrous metal portions develops couples which are particularly difficult to control with inhibitors. A solution to this problem is offered by 2-benzothiazolethiol which can inhibit attack on copper and its alloys to an extent such that negligible copper is dissolved by the water. The factors involved in the use of this material in conjunction with the glassy phosphate inhibitors for steel were investigated. It was found that 2-benzothiazolethiol showed a tendency to interfere with many glassy phosphates used to protect iron and steel; when the compound was used in connection with Calgon T this was not the case.

iron and steel with the glassy phosphates. Whereas a pH of 5 to 7 is *optimum*[1] for ferrous metals alone, the presence of copper narrows this range to 6.7 to 7.

Controlling the pH of circulating water within the narrow range of 6.7 to 7 is somewhat difficult, particularly because such waters are practically unbuffered in this region. The dissolved copper content of the water can build up rapidly when the pH falls below 6.7. Hence, even temporarily lower values are to be avoided. In many systems automatic pH control appears to be the only method by which values within this range can be maintained.

Occasionally the maintenance of a pH of 6.7 for the circulating water is not enough to prevent appreciable copper pickup. In a few isolated cases it was found necessary to raise the pH above the range where optimum protection of iron and steel with the glassy phosphates could be obtained in order to control dissolved copper.

The concentration of dissolved copper required to interfere with the protection of steel with the glassy

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[1] The glassy phosphates decrease the velocity of attack but do not alter the type thereof. The pH is a determinant factor with respect to the type of attack regardless of whether or not glassy phosphates are present. Thus, any attack which may occur tends to be general at pH values below 7 and to become progressively more localized as the pH is raised above 7. Consequently, pH values above 7 are less desirable because they tend to promote pitting and tuberculation. In addition, calcium phosphate sludge tends to become a problem in recirculating systems at pH values above 7. The efficacy of the inhibition decreases if the pH falls below 5.[1,3]

TABLE 1—Analyses of Tap Water Used (in PPM)

	Fig. 1	Fig. 2	Fig. 3, 4 & 5	Fig. 6, 7 & 8	Fig. 9, 11 & 12	Fig. 10	Fig. 13	Fig. 14
Calcium (as Ca)	25	15	19	49	55	17	18	19
Magnesium (as Mg)	5	8	5	19	17	4	4	7
Total Hardness (as CaCO₃)	86	74	67	200	207	58	62	77
Bicarbonate (as HCO₃)	20	18	18	10	4	12	12	18
Chloride (as Cl)	20	14	20	40	48	11	11	20
Sulfate (as SO₄)	81	53	48	180	224	62	56	80
Total Solids	200	206	148	368	424	136		176
Copper (as Cu)	0.02	<0.01	<0.01	<0.01	0.01	<0.01	0.02	0.01
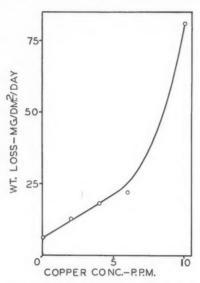
Figure 1—Influence of dissolved copper on the corrosion of steel in Calgon (50 ppm) treated water.

phosphates is quite low. The appearance of more than 0.1 ppm copper in a circulating water often is sufficient to indicate troublesome copper deposition. This is only a rough criterion of the quantity of dissolved copper required to exert a detrimental action because it represents the difference between the rate of pickup and that of redeposition. However, it does show that the rate of attack upon copper, which is involved, may be very low.

Alleviation of difficulties due to copper pickup by the water can be approached from two angles:

1) The resistance of the glassy phosphate film upon steel to the detrimental action of dissolved copper may be increased, and

2) The attack upon the cuprous metals may be inhibited to such an extent as to eliminate appreciable pickup of copper by the water.

Both approaches were subjected to preliminary investigation. The latter appeared the more promising and was checked more extensively.

Experimental

The laboratory data which will be considered were the results of small volume agitated batch tests of the type previously described.[1,(2)] Such tests require the use of higher concentrations of phosphate glass to obtain satisfactory inhibition than are needed in

practice—or, for that matter, in continuous flow or large volume batch tests.[1] This results from the limitation imposed on the rate of supply of glassy phosphate to the metal surface by the small volume of very dilute solution. The rate of formation of protective films on metal surfaces is a function of the rate of supply of inhibitor to these surfaces.

Ratios of calcium to glassy phosphate in the tests were within the range favorable for protective film formation. For the 1.1-sodium phosphate glass ($Na_2O : P_2O_5 = 1.1 :1$), Calgon, this range is a calcium:1.1-sodium phosphate glass ratio of 1:5 or greater.[1] This is identical to the standard recommendation for field applications.

Action of Dissolved Copper

The influence of dissolved copper on the inhibition of the corrosion of steel in Pittsburgh tap water (adjusted to pH 5.5) by the 1.1-sodium phosphate glass (50 ppm) is shown by the data in Figure 1. Extent of inhibition by the phosphate glass decreases as the copper concentration increases. Obvious copper deposits formed on the glassy phosphate treated plates quite early in these tests and remained visible for the duration of the tests (five days), particularly at the two lower copper concentrations where little rust formed to obscure or dislodge the deposits.

The data in Figure 1 do not show as marked a susceptibility, as field experience would indicate, of the protective glassy phosphate film to the deleterious action of very low concentrations of dissolved copper (of the order of tenths ppm). This appears to be due to the small volume batch nature of the test method employed. Formation of copper deposits on steel from waters which contain low concentrations of dissolved copper is a cumulative process. The deposits build up progressively as successive portions of the copper-bearing water contact the steel surface. The rate of formation of the deposit is a function of the rate of supply of dissolved copper to the steel surface. Thus, considerations somewhat similar to the formation of glassy phosphate films

(2) The salient features of this method are as follows: The test strips were 1½ x 1½-inch metal plates. The steel test panels were cold-rolled low carbon strips. Pittsburgh tap water adjusted to the desired pH with HCl served as the test medium. The analysis of the water used in the tests is shown in Table 1. Agitation was provided by lateral movement of the plates back and forth over a distance of two inches through one liter portions of water at a rate of 32 cycles/minute. The tests were conducted at 35 C ± 0.2. The metal plates were cleaned to a zero waterbreak in an alkaline cleaner prior to use. Copper test panels were pickled by a 10 percent nitric acid dip after the alkaline cleaning. At the conclusion of the tests where weight loss data were collected, the steel panels were pickled in 36 percent hydrochloric acid inhibited with 5 percent stannous chloride and 2 percent antimony oxide; the copper panels were pickled in 5 percent sulfuric acid. Pickling blanks were determined and the observed weight losses corrected accordingly.

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should apply to the formation of copper deposits;
i.e., a higher concentration of dissolved copper would
be expected to be required to affect the protective
action of the glassy phosphate film in a small volume
batch test than in an actual recirculating system.
This is true particularly because the copper content
of the water in the latter case would be replenished
with each pass through the cuprous metal portions
of the system.

Appearance of panels exposed to copper-bearing
waters treated with glassy phosphate provides a clue
to the apparently anomalous behavior of these in-
hibitors with couples formed by the junction of
steel and copper members as contrasted to those
formed by the deposition of dissolved copper upon
steel. Low concentrations of dissolved copper cause
a darkening of the metal surface. Interference colors
characteristic of the glassy phosphate film on a smooth
surface are evident, but they appear as though they
were placed on a dark background rather than on the
bright steel surface. Scattered rust spots are present
which apparently emanate from breaks in the pro-
tective film.

The deposit at the higher dissolved copper con-
centrations is a dull, very dark red and rather
powdery. Such deposits seem loosely adherent and
often flake off from the steel surface on drying. Cor-
rosion of the steel which proceeds under these de-
posits often gives the appearance of raising this
powdery coating in small tubercules during the early
stages of the attack. Water apparently seeps through
the copper deposit and permits galvanic attack of the
underlying steel.

The diffusion of hydrogen (and perhaps oxygen)
through this layer apparently is sufficient to de-
polarize the cathode and permit attack on the steel
to proceed. The underlying surface of the copper
deposit appears to be the cathode involved in the
galvanic attack of the steel base. Apparently the
glassy phosphate does not diffuse through the rather
porous copper deposit quickly enough to form a
film on its underlying surface which will effectively
polarize this cathodic area of the cell. (Diffusion has
proved insufficient to supply glassy phosphate to the
metal surface in quantities adequate for protective
film formation with threshold concentrations (i.e.,
1 to 100 ppm) of these phosphates.) Thus, galvanic
cells formed by deposition of dissolved copper on
steel appear to be formed in such locations that the
glassy phosphate does not have access to surfaces
actively involved.

Influence of Phosphate Inhibitors on Copper Deposition

Several molecularly dehydrated phosphate inhibi-
tors were tested and found to have no appreciable
influence on the rate of deposition of copper on steel
from a 2 ppm solution[3] (pH=5.5). The materials
checked (at concentrations of 50 ppm) were the 1.1-
sodium phosphate glass, Calgon T (i.e., a sodium
zinc phosphate glass), tetrasodium pyrophosphate
and a 60 percent 1.1-sodium phosphate glass—40 per-
cent sodium dichromate mixture. The data obtained

[3] Copper was determined colorimetrically as the diethyldithiocarba-
mate after extraction of this salt from a citrate buffered solution
at pH 9.5 with carbon tetrachloride.
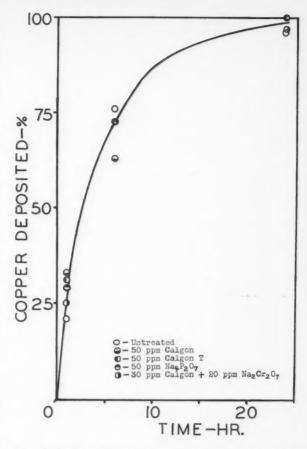
Figure 2—Deposition of copper on steel in the presence (and absence) of several phosphate inhibitors for steel.
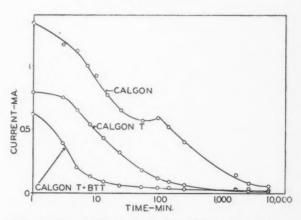
Figure 3—Rates of reduction of galvanic attack on steel coupled to copper with Calgon (50 ppm), Calgon T (50 ppm) and Calgon T (50 ppm plus 2 ppm of benzothiazolethiol.)

are shown in Figure 2 wherein a single curve suffices
to represent data for all of these inhibitors as well
as for the untreated system. None of these materials
show an appreciable effect on the rate of deposition
of dissolved copper on steel. (Similar tests were con-
ducted in which a copper precipitant, sodium ferro-
cyanide, was included. It caused a slight initial lag

Figure 4—Influence of benzothiazolethiol concentration on the corrosion of copper in Calgon T (50 ppm) treated water.

Figure 5—Influence of benzothiazolethiol concentration on the pickup of copper from the metal by Calgon T (50 ppm) treated water.

Figure 6—Influence of pH on corrosion of copper in Calgon (50 ppm) treated water and the effect thereon of benzothiazolethiol (5 ppm).

but the subsequent deposition proceeded at about its normal rate.)

Deposition of copper takes place rapidly and a good portion thereof probably occurs before the protective film formed by the 1.1-sodium phosphate glass is fully developed. However, acceleration of the formation of a protective film on steel does not appear to be a particularly promising means of solving the copper deposition problem especially in view of the results obtained with Calgon T. The protective character of the film develops considerably faster with this zinc-bearing glass than with the sodium glass (see Figure 3). This is the chief reason for incorporation of zinc in the glass.

Inhibition of Copper Corrosion

Perhaps the most direct approach to solution of the problem raised by pickup of copper from the system and its subsequent deposition on steel would be protecting copper and its alloys so negligible pickup would occur. Such a solution has the added practical advantage that it provides more positive protection to the cuprous portions of the system.

Quantities of dissolved copper which limit the inhibition of the steel are so low they do not necessarily imply appreciable decrease in the life of the copper equipment. However, corrosion of the cupous portions of water systems occasionally becomes sufficient to cause failures.

2-benzothiazolethiol[4] was found to satisfy the first of these requirements in that it reduces the attack upon copper to an extremely low level. However, this compound shows a tendency to interfere with the protective action of most of the glassy phosphates used to protect iron and steel. However, the zinc-bearing phosphate glass, Calgon T, is not subject to this interference. Thus, BTT (i.e., 2-benzo-

thiazolethiol) used with Calgon T permits operation throughout the optimum pH range (i.e., 5 to 7) for protection of iron and steel with the glassy phosphate regardless of the presence of copper or its alloys in the system. The commercial product, Coraid furnishes both BTT and zinc, hence may be used with 1.1-sodium phosphate glass without interference with the protective action of the glassy phosphate film on iron and steel. It yields practically the same results as the combination of BTT and Calgon T.

The influence of BTT on the corrosion of copper in Pittsburgh tap water (adjusted to pH 5.5) treated with 50 ppm Calgon T is shown by the data in Figures 4 and 5. The former shows its influence on the weight loss and the latter its effect on the copper picked up by the water. The data show that two ppm BTT suffices to reduce both the weight loss and the copper pickup to values too low to be detected by the analytical procedures[4] which were used (i.e., less than 0.1 mg/dm²/day and 0.01 ppm, respectively).

Considerations Involving pH. Data in Figure 6 show BTT is effective at low pH values. 5 ppm prevents detectable weight loss of copper in water treated with Calgon T (50 ppm) at pH values as low as 3. Analyses of BTT treated waters at the conclusion of the 5-day tests showed no dissolved copper at pH values down to 3. These results show that BTT is a very effective inhibitor of copper attack at pH values considerably below the minimum recommended in conjunction with the use of glassy phosphates for protection of iron and steel (i.e., pH 5). They are of interest in that they indicate that the inhibitor would be effective for the reduction of copper pickup in cases where the pH of a system was lowered temporarily, either purposely to facilitate removal of old deposits or accidentally because of acid leakage.

[4] BTT in the concentrations to be considered exerts no interference with the analytical method employed for the determination of copper.
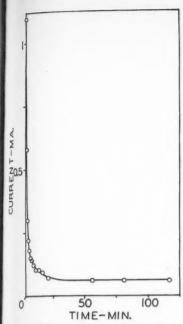
Figure 7—Rate of reduction of galvanic attack on steel coupled to copper with benzothiazolethiol (2 ppm).
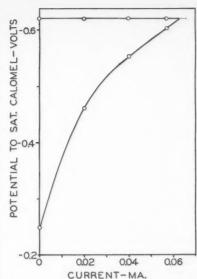
Figure 8—Polarization of copper and steel coupled in benzothiazolethiol (2 ppm) treated water.
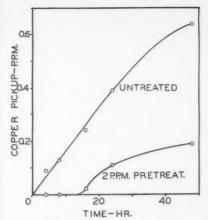
Figure 9—Influence of benzothiazolethiol (2 ppm) pretreatment on the subsequent pickup of copper by untreated water.

Rate of Film Formation. Formation of a protective film upon copper is quite rapid with BTT—considerably faster than film deposition upon copper coupled to steel by either Calgon or Calgon T. This is illustrated by the data in Figure 3 which shows the influence of 50 ppm Calgon, 50 ppm Calgon T and 50 ppm Calgon T + 5 ppm BTT, respectively, on the current flow between copper and steel plates[5] at pH 5.7 as a function of time. (The latter was plotted on a logarithmic scale in order that the widely different rates of current decrease for these three systems could be included in a single figure.) Comparison of the rates of formation of the protective films is facilitated perhaps by consideration of the times required to attain a particular low current value. The times required to reach a current of 0.1 ma which corresponds to a galvanic corrosion rate of 8.6 mg/dm²/day are as follows:

50 ppm Calgon......................2180 minutes
50 ppm Calgon T..................... 145 minutes
50 ppm Calgon T + 5 ppm BTT....... 12.5 minutes

These data show that protective film formation is considerably more rapid when BTT is present than with either of these phosphate glasses alone, even in couples where the latter have free access to the surfaces involved.

The data in Figure 3 also illustrate the more rapid film formation with Calgon T than with the 1.1-sodium phosphate glass which was mentioned earlier in conjunction with the discussion of Figure 2.

The discontinuity in the curve for the 1.1-sodium phosphate glass in Figure 3 is similar to those occasionally observed previously[2] for this system. It appears to be due to a shift of the open-circuit potential of the steel in an anodic direction. The value of the open-circuit potential of the steel at the conclusion of the test in question tended to confirm this shift.

Action. The very rapid reduction in current flow in the BTT treated system (Figure 3) appears to be due to the action of this thiol on the copper cathode. Further, this action seems to be rather specific for copper and its alloys because BTT shows no similar action in systems with steel or stainless steel (Type 302) cathodes. The reduction in current flow in the systems treated only with the glassy phosphates (Figure 3) also is due primarily to action on the copper cathode; the film deposited thereon greatly increases the polarization.[2,5] (The glassy phosphate films are laid down by a process of electrodeposition and are much heavier on copper cathodes than would be the case with uncoupled copper panels.[5])

More definite evidence of the action of BTT is provided by tests with this material alone (i.e., where other compounds, such as the glassy phosphates, which increase polarization of the copper cathode are absent). Figure 7 shows the current from a copper-steel couple in a water (pH = 5.5) treated with 2 ppm of this thiol as a function of the time. (The curve for a parallel test with an untreated system rose from 1.2 to 1.6 ma during the time interval covered in this figure. For most of the period the current was higher than the range included in Figure 7.) It is evident that BTT alone causes a very rapid drop in the current flow. Results of polarization tests of this system run after two hours are included in Figure 8. The upper arm of this curve shows the potentials of the steel anode and the lower those of the copper cathode. The dotted line shows the short circuit potential of the couple. These data show that the decrease in current caused by the thiol is due to

Figure 10—Influence of benzothiazolethiol concentration on the corrosion of steel in Calgon (25 ppm) and Calgon T (25 ppm) treated water.

Figure 11—Influence of benzothiazolethiol (5 ppm) on the current from differential aeration cells (steel electrodes) in Calgon (25 ppm) and Calgon T (25 ppm) treated water.

Figure 12—Influence of benzothiazolethiol (5 ppm) on the polarization of differential aeration cells (steel electrodes) in Calgon (25 ppm) and Calgon T (25 ppm) treated water.

a marked polarization of the copper cathode. The steel anode shows no appreciable polarization in this test. The high polarization of the cathode apparently is the result of an absorbed or chemisorbed film of the BTT on the copper surface.

BTT alone markedly inhibits the galvanic attack of steel in this couple (Figure 7). However, it does not appear to retard the nongalvanic portion of the attack because the steel corrodes to about the same degree as an uncoupled panel would in untreated water. (Additional tests with steel panels alone showed no appreciable inhibitive action of BTT in concentrations up to 25 ppm.) The continued corrosion of the steel panel appears to interfere with the action of the thiol on the copper cathode. After several hours exposure to water treated *solely* with the thiol the protective film on the copper starts to deteriorate and the current from the couple gradually rises. For this reason tests to investigate the action of BTT alone were brief.

Resistance to Untreated Water. The protective film deposited on copper in water treated with BTT shows considerable resistance when exposed subsequently to water which does not contain this inhibitor. Figure 9 shows the influence of pretreatment of copper strips for one hour with 2 ppm BTT and 50 ppm Calgon on the subsequent pickup of copper from these strips by untreated Pittsburgh tap water (adjusted to pH 5.5). Data for a strip pretreated with 50 ppm Calgon alone is included for comparison. The film formed by the BTT affords practically complete protection for 17 hours after discontinuance of the treatment but after this copper pickup increases gradually. (A similar test with BTT pretreatment at the rate of 5 ppm gave results which were identical, within the limits of experimental error, to those obtained at 2 ppm.)

Effect on Phosphate Films. The interference of BTT

with the protective film of glassy phosphate mentioned earlier is somewhat erratic from a quantitative point of view. The degree of interference varies somewhat in duplicate tests. However, elimination of the interference by using zinc-bearing phosphate glass is not erratic. Typical data which show the interference (to an approximately average degree) as well as its elimination by the use of Calgon T are included in Figure 10. These data show the influence of thiol concentration on the corrosion of steel in Calgon (25 ppm) and in Calgon T (25 ppm) treated water (pH = 6.5). The corrosion rate in the Calgon treated water increases as the concentration of BTT is raised, whereas the BTT has little effect on the corrosion of steel in the water treated with the zinc-bearing glass.

Differential aeration tests[6] were conducted to gain further insight concerning the interference of BTT with the glassy phosphate film as well as the reason for its lack of interference with the zinc-bearing glass. Figure 11 shows the influence of BTT on the current flow from differential aeration cells with steel electrodes in water (pH = 6.5) treated with the two phosphate glasses. The current from the system treated with both Calgon and BTT (5 ppm) drops off rapidly at the start, but rises later and levels off at a much higher value than in the test with Calgon alone. The curve for the system treated with Calgon T (25 ppm) and BTT (5 ppm) falls off rapidly and levels off at a low current value indicating that the BTT does not interfere with reaching the low current flow.

Polarization data for these tests (after a 48-hour run) are shown in Figure 12. The upper arms of these curves represent the potentials of the anodes (i.e.,

[6] The differential aeration cells and the test procedure employed were described previously.[5] The cells consisted of parallel steel plates (0.28 dm²) separated by a distance of 0.5 inch. One of the plates (i.e., the anode) was covered with Whatman No. 120 paper to restrict access to dissolved oxygen; the other (i.e., the cathode) was not covered.

the covered plates) and the lower the potentials of the cathodes (i.e., the bare plates). These data indicate that the chief cause for the higher current which results from the use of BTT with Calgon is the higher potential difference of the cell; the polarization of neither electrode (as represented by the slopes of the corresponding curves) is altered appreciably by the BTT. The higher potential difference in turn is primarily the result of the greater cathodic potential of the bare steel member of the couple (i.e., the cathode). Thus, the BTT inhibits the shift in potential of the bare steel plate in an anodic direction which is characteristic of Calgon alone[5] and is one of the major factors responsible for the decrease in current flow from differential aeration cells treated with this inhibitor (the other is the increased cathodic polarization). The BTT does not have a like action with the zinc-bearing glass, so the current attains a low level despite the thiol.

Galvanized Steel. Galvanized steel occasionally is used together with copper and its alloys in small recirculating systems, as in certain air conditioning equipment. Dissolved copper content as high as 93 ppm has been reported in untreated circulating waters of air conditioning systems.[6] As little as 0.1 ppm dissolved copper has been reported to increase the attack on zinc.[7]

The influence of dissolved copper on the corrosion of zinc strips in Pittsburgh tap water is shown in Figure 13 (pH = 6.5). 0.1 ppm causes a considerable increase in the rate of attack on the zinc even in these small volume laboratory tests. Thus in the absence of inhibitors traces of copper appear to have a much more marked influence on the corrosion of zinc than of steel. This may be due to some extent to the lower rate of attack of the zinc by the untreated water (i.e., the copper may remain longer on the zinc surface before it becomes dislodged and entangled in a layer of corrosion products). The rather low rate of attack on zinc by the untreated tap water (35 C) seems somewhat at variance with the performance of galvanized pipe in domestic service with this water. The cause for this apparent anomaly may lie in the rather indiscriminate use of galvanized pipe along with copper and its alloys in many domestic installations. Water drawn from copper lines often contains traces of this metal which are sufficient to cause high rates of attack of zinc.

The influence of BTT on the weight loss of uncoupled zinc and copper strips immersed together in Pittsburgh tap water is shown in Figure 14. The attack on the zinc strip decreases as the concentration of BTT rises to 2 ppm, while further increases cause a very slight increase in the corrosion rate. Perhaps the most significant feature of these data is that the low level of attack on the zinc is attained at the same BTT concentration required virtually to eliminate attack on the copper. The two lower concentrations of BTT reduced attack on the zinc even though they did not affect appreciably the weight loss of the copper. However, the weight loss reflects the quantity of copper in the corrosion products which adhere to
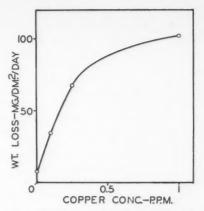
Figure 13—Influence of copper concentration on the corrosion of zinc.
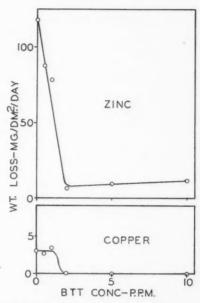
Figure 14—Lower curve shows the influence of benzothiazolethiol concentration on the pickup of copper from a copper strip. Upper curve shows the influence of benzothiazolethiol on the corrosion of a zinc strip immersed in the same water (uncoupled).

the copper plate as well as the quantity which goes into the water.

Discussion

It was mentioned above (i.e., in conjunction with the data in Figure 7) that BTT alone did not inhibit appreciably the nongalvanic portion of the attack on steel coupled to copper. This point was subjected to further test because BTT has been used as an inhibitor for iron and steel[8] under conditions different from those in tests reported here or in recirculating cooling systems. Concentrations of BTT up to 25 ppm—a much higher concentration than would be required for control of copper corrosion—provided no appreciable protection to steel in Pittsburgh tap water at pH values of 5.5 or 6.5.

The commercial product, Coraid, used with Calgon has given field results similar to those obtained in the laboratory with Calgon T and BTT. It has been particularly helpful in systems where the pH could not be controlled closely enough to prevent appreciable pickup of copper by the circulating water with the result that adequate protection of iron and steel with the glassy phosphate alone could not be attained. The application of Coraid to these systems has practically eliminated the copper pickup (i.e., copper contents of the recirculating waters run from 0 to 0.02 ppm) with the result that good protection of the iron and steel with the phosphate glass is obtained. Moreover, the pH in these systems has been decreased to 6.0 — 6.5 and no longer is a critical consideration.

Coraid also has reduced copper pickup in systems where pH control alone was unsuccessful despite very close control. Copper content of 0.2 to 0.4 ppm persisted in the circulating water of an oil refinery in spite of accurate pH control in the range of 6.8 to 7. The use of Coraid permitted a drop in the pH to 6 and reduced the copper content to such a level it could not be detected by the analytical procedure used (i.e., to less than 0.01 ppm).

Acknowledgment

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Any discussions of this article not published above will appear in the December, 1955 issue.

DISCUSSIONS ON TECHNICAL ARTICLES ARE SOLICITED

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A Technical Note

Corrosion of Lead-Lined
Sulfuric Acid Evaporators*

By W. J. COTTON

TWO cases involving the failure of lead linings in sulfuric evaporators were investigated recently and the causes of failure determined. The two cases differed markedly both in the cause of failure and in the corrective measures adopted. A brief account of each incident is given below.

Case 1

The first case involves a midwestern plant which operated eight 13-foot diameter lead-lined sulfuric acid evaporators. The engineering department of the company kept excellent records on the maintenance and life of the evaporators. The lead linings approximated 370 mils when new and had been purchased from the same manufacturer; it was found, however, that this manufacturer operated two plants.

An examination of the records showed that the sheet lead supplied by Plant A of the manufacturer gave consistently longer life than did the sheet lead supplied by Plant B. The time for the Plant A sheet was seven years as compared to 18 months for the Plant B sheet.

Several samples each of sources from A and B were submitted to analyses. In making the analysis, even minute traces of non-lead components were determined. Although lead in all cases made up more than 99 percent of the total, traces of about a dozen other metals also were found. The two groups of samples gave substantially identical average analyses. Any differences registered were altogether too minute to be suspected as the source of the trouble.

Polished and etched samples were submitted to microscopic examination. It was found that the sheet lead from Plant B consistently showed a crystalline structure wherein the crystals varied greatly in size, some crystals having a surface area fifty to sixty times the surface area of the smaller crystals. Furthermore, the small crystals appeared to be anodic to the large crystals as the pinholes in the corroding sheet appeared to be at the location of the small crystals.

On the other hand, a photographic examination of the sheet of Plant A showed an almost complete lack of crystalline structure.

It is believed that in the manufacture of sheets, Plant B did not cool or chill the sheet with sufficient rapidity to prevent crystallization. At Plant A, however, the sheet appeared to have been cooled very rapidly. This resulted in solidification of the metal

W. J. COTTON is owner and manager of the W. J. Cotton Laboratories, Milwaukee, Wisconsin. He received a BA degree in 1910 from Ripon College and a year later an MS degree from the University of Wisconsin; at both schools he majored in chemistry and chemical engineering. His experience includes five years of college and university teaching; three years as Chief Chemical Examiner, United States Civil Service Commission; 15 years as group leader of the Research Department, National Aniline & Chemical Co., Buffalo, N. Y.; six years as group leader of the Research Department, Monsanto Chemical Co., St. Louis, Mo.; and seven years as research director, Pennsylvania Coal Products Co., Petrolia, Pa. In recent years he has served many clients as a consulting chemist and chemical engineer. Mr. Cotton is a member of a large number of technical organizations, including NACE.

Abstract

Two cases involving failure by corrosion of lead linings in sulfuric evaporators are reported. Case 1 involved an investigation of the reasons for a difference in service life of almost four to one between sheet supplied by two plants of the same manufacturer. The investigation showed the sheet failing in 18 months had a crystalline structure in which some crystals were 50 to 60 times greater in surface area than others. The smaller crystals appeared to be anodic to the large ones as pinholes in the sheet appeared to be at the location of the small crystals. The other sheet, which lasted seven years, was found to lack crystalline structure almost completely, indicating proper cooling technique.

Case 2 involved rapid disintegration of the lining of an evaporator into which prevailing winds introduced abrasive dusts from a nearby steel mill. It was postulated and proved in laboratory tests that the abrasive continuously removed the protective lead sulfate coating. When the evaporator was enclosed to exclude the dust, the trouble disappeared.

and the consequent formation of a highly uniform, very fine grained structure.

The purchase of non-crystalline sheet appears to be the solution to the problem of lead failure in Case 1.

Case 2

The sulfuric acid evaporator involved in Case 2 was used to recover spent acid which resulted from nitration operations in an eastern chemical plant. The evaporator was housed in a standard factory building and equipped with a forced draft fume stack. It has been in operation for many years; an occasional patching of lead lining was needed and a

complete reline job was required about every ten years, company records indicated.

Because the building and area were needed for other operations, it was decided to relocate the evaporator a mile away on a point that projected out into a river. It also was decided that the modern type of factory building construction would be used; namely, a building without sides, but with a roof through which fumes could be vented by means of a stack with forced draft. There were no buildings of any description in the immediate vicinity.

Trouble was experienced in the new location from the very beginning. The linings disintegrated rapidly. Lead sulfate sludges became quite objectionable and for the first time considerable sulfur dioxide gas was noted. The question was why.

A two gallon lead-lined evaporator was built for test work in the laboratory. The same stock of sheet lead was used in lining it as was used for the large evaporator. Samples of the tank wagon loads of spent acid going to the large evaporator were taken to the laboratory for evaporation tests.

No difficulty was experienced in the laboratory. There was a negligible amount of wear on the lead; the amount of sulfur dioxide formed after the initial decomposition of the organic matter also was negligible.

A close observation of the plant operation revealed that more difficulty was experienced when the wind was from the west than when it was from any other direction. The prevailing winds, however, were from the west most of the time. About a half mile to the west were the stacks of a steel plant. The question arose as to whether there could possibly be enough abrasive dust carried by the prevailing winds from the stacks to continuously erode or abrade the protective coating of lead sulfate.

Some two grams of filtercel were added to the laboratory evaporator along with the usual sample of spent acid. It should be noted that both the plant and laboratory evaporators were provided with mechanical agitation. Upon adding the filtercel, the laboratory evaporator began to evolve hydrogen gas admixed with sulfur dioxide to such an extent that an explosion hazard almost was created. Apparently the filtercel continuously abraded the protective coating of lead sulfate.

The next thing done was to move the laboratory evaporator to a spot closely adjacent to the relocated plant evaporator. Here difficulty was experienced with the laboratory evaporator, although not to the extent as in the laboratory after filtercel was added.

The results of these tests led to the conclusion that there was enough abrasive dust in the air, particularly when carried from the steel mill stacks by the prevailing winds, to cause trouble. It should be noted that the air *appeared* to be clear and dust free. It was found, however, that a cotton pad placed on a suction funnel blackened all the same.

It was recommended that the evaporator be enclosed by a standard type of building construction. After this was done no further significant evaporator difficulty was experienced.

Any discussions of this article not published above will appear in the December, 1955 issue.

Corrosion Control on Offshore Drilling and Producing Equipment*

By CHARLES J. FRITTS

1. Offshore Operations, General

OIL COMPANIES are pushing farther out to sea and into deeper water all the time in their search for oil. To accomplish their drilling and producing operations requires much more equipment than land-based operations of the same scope. For most far-offshore operations a platform of some type must be built for the drilling rig. These are usually built of steel, although both wood and pre-stressed concrete have been used to some extent. Wood is a good material from the corrosion resistance standpoint, but it presents a fire hazard which offsets any other advantages it may have. Pre-stressed concrete pilings are being developed to the point where they can be used successfully in deeper water. They should be very good for corrosion resistance, providing the concrete is impermeable enough to prevent corrosion of the stressing wires.

Drilling platforms are expensive. A smaller platform where a drilling tender will be used costs from $300,000 to $500,000 in place. The larger self-contained platforms may cost from $1,000,000 upward. Drilling tenders also are in the million dollar class. Offshore operations require a fleet of boats for transportation of men and equipment.

Almost all platforms and floating equipment are of steel and therefore are subject to corrosion. There are known today means of preventing corrosion of this equipment but it remains for the corrosion engineer to apply them to best economical advantage.

2. Platforms

A. *Corrosive Areas and Corrodants*

There usually are considered to be three zones of varying corrosiveness on offshore platforms: The atmospheric zone, where the steel is subject to corrosion by high humidity and some degree of salt spray; the splash zone near the water line where the steel is in contact with spray and is alternately wet and dry depending on weather conditions; and the submerged zone where the steel is continually wet by salt water. Of these, the splash zone is the most corrosive and it is toward this zone that most of investigative efforts are directed now.

In 1950, specimens were cut from a salvaged bumper dolphin and a platform which had been in the Gulf of Mexico 1½ years. On the basis of weight loss of these specimens, the overall average corrosion rates of steel at varying distance above and below the water line were calculated and a corrosion rate profile plotted from these values as shown in

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CHARLES J. FRITTS—Presently sales representative for Socony Paint Products Co. for Houston and South Texas areas, he has been concerned with corrosion control since 1949. From 1952 to 1954 he was corrosion engineer on the Magnolia-Continental-Newmont offshore operations at Morgan City, La. He joined Socony in July, 1954. He has a BS in industrial chemistry from University of Kentucky, 1947. Prior to that he was employed by the Formica Insulation Co. and by Joseph E. Seagram & Sons in operations. He joined Magnolia's Field Research laboratories in Dallas after graduation and spent two years on the chemistry of drilling muds.

Abstract

Steel piling is preferred for offshore stationary drilling platforms because wood creates a fire hazard and stressed concrete may fail if salt water penetrates to the stressed reinforcement. Methods used by one oil company to protect its platforms are described.

Specific recommendations are made for the three areas into which the platform is divided with respect to corrosion and for tenders and boats used in operations. For the atmospheric zone 10 or more feet above the water line a 6-coat minimum 6-mil vinyl system is recommended. Epoxy and hot spray vinyl systems are under test but not yet evaluated.

In the splash zone, from the water line upward 10 feet, design placing horizontal and diagonal bracing above or below this zone is recommended. Choice of methods of protecting this, the most corrosive zone, depends on the intentions of the company with respect to permanence of the platforms and other factors. Mentioned by the author, with costs per square foot are Gunite, Monel, porcelain enamel, sheet Neoprene, flame-sprayed polyethylene, plastic tapes over vinyl, metalizing, vinyl mastic systems and protective jackets.

Protection of submerged zone areas on fixed and floating surfaces by cathodic protection is recommended. Methods of using magnesium anodes are described. Bonding platform and tender when tender houses welding machine positively grounded to the tender is recommended.

Figure 1. The dolphin had not been painted when placed in the Gulf, but the platform had been painted with a system of unknown type and brand which had partially failed at the time the specimens were cut. Neither the dolphin nor the platform was under cathodic protection during the period of exposure.

1. Atmospheric Zone. This zone usually is considered to be higher than 10 feet above the water line. Corrosion in the atmospheric zone can be controlled adequately with organic coatings. A coating system for use on drilling platforms, in addition to providing a vapor barrier, must be capable of resisting both the

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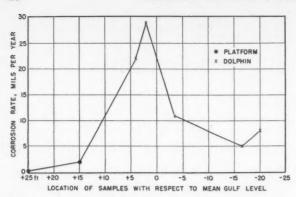
Figure 1—Corrosion rate profile plotted from weight loss of specimens cut out of platform and bumper dolphin which had been in the Gulf of Mexico 1½ years.

Figure 2—A type of recirculating paint heater used in application of hot-spray vinyl system.
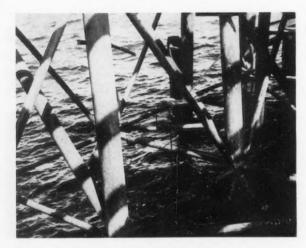
Figure 3—An example of a poorly designed platform from the corrosion engineer's standpoint. Necessary bracing should be placed either above or below the splash zone.

caustic drilling muds whose pH runs as high as 13 or 14 and the occasional spillage of Diesel fuel and crankcase oils. A 6-coat vinyl system consisting of a wash primer, a zinc chromate primer, three build coats and one top coat has been found to give excellent performance in this zone when applied to a minimum thickness of 6 mils.

Both epoxy coatings and hot spray vinyl coatings are under test on equipment in the Gulf, but this

equipment has not been in place long enough for predictions to be made concerning the expected life of the systems. A bumper dolphin was coated with an epoxy system over a butyral wash primer and placed offshore in May, 1954. This system failed near the water line in approximately six weeks, the epoxy separating from the wash primer, although in the atmospheric zone of the dolphin the system was still in perfect condition at the end of six months. It is possible that the failure was caused by the phosphoric acid in the wash primer reacting with the amine catalyst at the epoxy-wash primer interface and preventing proper bonding between the two materials.

Hot-spray vinyl coatings are formulated in a manner similar to the ordinary cold-applied vinyl, except that solvents of lower volatility are used. A higher concentration of vinyl resin can be used, since the viscosity is reduced to spraying consistency by heating rather than by the addition of thinner. These materials are applied at a temperature of from 150 to 170 F. Figure 2 shows one type of heater which has proved very satisfactory for use with the application of hot-spray vinyl. It is electrically operated and continuously recirculates heated material to the gun. The thermostatic control is set for 160 when vinyl is used. The advantages of the hot-spray application of vinyl are: Greater thickness of vinyl can be applied per coat without runs or sags; it is not necessary to add additional thinner, which results in a saving on material purchased; and variations in viscosity and temperature of the coating material at the gun are eliminated. Its disadvantages are: working with the hot-spray equipment is somewhat more cumbersome than with ordinary equipment, since the hose length between the heater and the gun is limited to approximately 30 feet; the solvents in the hot-spray vinyl must be of lower volatility, therefore the hot-spray vinyls dry more slowly than do the cold-applied vinyls; and most of the applicators are not familiar with these materials, because they are fairly new on the market in the Gulf Coast area. Approximately 50 different coating systems are under test on panels on a platform 28 miles from shore. These systems were applied under field conditions in Magnolia Petroleum Company's Morgan City, La., yard.

2. **Splash Zone.** This zone extends from the water line upward approximately 10 feet. If necessary horizontal and diagonal bracing is placed either above or below the splash zone protection of this zone is greatly simplified. An example of improper design is shown in Figure 3.

Although there are many solutions to the problem of corrosion in this zone, all are somewhat expensive when compared to the cost per square foot of protecting the remainder of the platform. To a great extent, the choice of a method of protecting the splash zone depends on the proposed service for the equipment. Some systems under test in the Gulf which appear to have possibilities of performing well in the splash zone are as follows:

a. *Gunite.* ($1.50 per sq. ft.) This sprayed concrete

coating has given excellent service where it is not subjected to damage by boats. The living quarters platform shown in Figure 4 has been in place since March 1951 with no indication of deterioration of either the gunite or the steel of the platform. After one year in service, specimens were cut out of the gunite and examined. The concrete was well bonded to the reinforcing and showed a permeability of from 2.5 to 5.0 microdarcies. Gunite is easily damaged and where there is danger of it being rammed by boats or where the additional weight of the concrete will overload lifting equipment, some other material should be chosen. One advantage of this material is that it can be applied to platforms already in place in the Gulf.

b. *Monel.* ($5 to $7 per sq. ft.) Several platforms were jacketed in the splash zone during construction with 16-gauge "B" Monel. This Monel is formed into cylindrical jackets which are slipped over the platform members and welded at the top and bottom to form a watertight seal (Figure 5). If properly applied, the Monel can withstand severe blows without tearing. Monel jacketing probably is the best known method of protecting the splash zone if a platform is to be at the same location for a number of years. It would not be economical to use Monel on a platform which would be moved to another location of different water depth in a short time, although the cost of Monel would be well justified for a platform used for drilling in a proved field.

c. *Porcelain Enamel* ($3-$5 per sq. ft., estimated). Two 10-foot lengths of 20-inch pipe were enamelled and installed as vertical members in the splash zone of a platform. One specimen is on the outside of the platform where it is exposed to floating equipment. The other is inside the platform where it is protected against damage. Both specimens were still in perfect condition after 9 months in service, except for slight damage by weld spatter which occurred during installation and which could have been avoided easily.

d. *Sheet Neoprene* ($3 per sq. ft.). 1/16 inch sheet Neoprene was cemented to one of the 20-inch vertical members. The metal was first sand blasted, then a special primer was applied and allowed to dry. Two coats of a bonding agent were applied over the primer and allowed to dry. One coat of the bonding agent was applied to the back of the Neoprene sheet. The sheet was then pressed tightly against the steel and rolled to insure good contact. Bubbles which remained behind the sheet were removed by puncturing the sheet with a hypodermic needle (Figure 6), then sealing the resulting pinholes with the bonding agent. The sheet was applied in two sections and the seams were overlapped. The areas at each end of the sheet were given two coats of liquid Neoprene.

e. *Flame-sprayed Polyethylene* ($2 per sq. ft.). Polyethylene is very resistant to moisture vapor penetration. Heretofore the disadvantage of this material has been its lack of adherence. Now, a wash primer is used under the plastic which is supposed to bond

Figure 4—Gunite in splash zone of living quarters platform which has been in place since March, 1951.
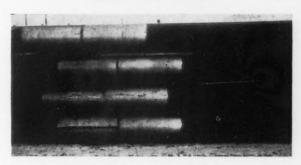
Figure 5—Monel jacketing in splash zone of vertical members prior to fabrication of platform.

Figure 6—Removing air bubbles from behind Neoprene sheet by puncturing with hypodermic needle. Resulting pinholes are sealed with Neoprene bonding agent.

well with the polyethylene yet not be decomposed during the preheating of the metal prior to spraying. The polyethylene is in the form of a fine powder which is fed from a dispenser to the gun by means of compressed air. The powder is melted by an oxyacetylene flame as it passes through the gun. The particles hit the metal surface in a molten condition and adhere to form a smooth coating. The resulting film thickness on one test section was 30 mils. Although this section had been damaged during setting of the platform, at last inspection after nine months' service there was no indication of undercutting.

Figure 7—Vinyl tape in splash zone of offshore platform after one year exposure in the Gulf.
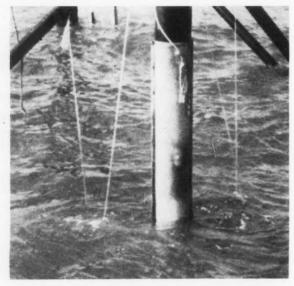
Figure 8—Tidal zone protective jacket in place on small platform.
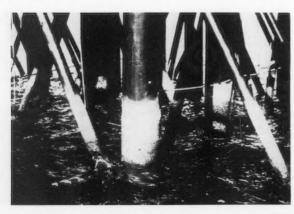
Figure 9—Splash zone of offshore platform showing calcareous coating which builds up when platforms are under cathodic protection.

f. *Plastic Tapes Over 6-coat Vinyl System* ($0.90 per sq. ft.). 10-mil polyethylene and 20-mil vinyl types were applied over the standard 6-coat vinyl system to give added resistance against abrasion in the splash zone. At last inspection the polyethylene had lost adherence where crankcase oil had run down on it. The vinyl tape was still in perfect condition (Figure 7).

g. *Metallizing* ($0.95 per sq. ft., estimated). Both zinc and aluminum metallizing of 15-mil thickness are under test. The aluminum was applied over a "flash coat" of steel. Both of these materials were in excellent condition after nine months' service.

h. *Vinyl Mastic System* ($0.80 per sq. ft.) Approximately 1/16 inch of a vinyl mastic was applied over the conventional 6-coat vinyl system to give added resistance against abrasion in the splash zone. At last inspection this material was in excellent condition. This promises to be an economical system for protecting the splash zone of structures which may be moved to other locations if no oil is found. Vinyl mastic by itself does not have sufficient impermeability and the conventional vinyl system does not have sufficient abrasion resistance to give adequate service in the splash zone. However, each of these materials complements the other and the combination system should perform well.

i. *Tidal Zone Protective Jacket* ($3.00 per sq. ft.). A jacket made of fiberglass-reinforced polyester plastic has been developed for clamping around a member in the splash zone. The top and bottom are sealed by neoprene gaskets. After installation, the jacket is pumped full of a grease-type material to insure that water will be excluded. One of these jackets has been in place on a small platform (Figure 8) for approximately six months. The jacket itself shows no signs of deterioration at this time.

3. **Submerged Zone.** The submerged zone of a platform can be protected best by the use of cathodic protection. In sea water, cathodically protected steel quickly builds up a calcareous coating (Figure 9) which cuts down the current required to maintain an adequate potential (—0.85 volts with respect to a saturated calomel electrode) and also in itself acts as a protective coating for the steel. This coating is composed primarily of calcium carbonate and magnesium hydroxide, the proportion of each depending on the current density at the time the coating is formed.

a. *Anodes Are Used.* Magnesium anodes are used exclusively by Magnolia Petroleum Co., for cathodic protection of offshore platforms. As a rule of thumb for designing the systems, one anode is used for every 1200 square feet of steel submerged in the sea, one anode is used for every 2400 square feet of steel submerged in the mud, except for all casing below 1000 feet, which is neglected. Systems of this type have a life of approximately two years before replacement of the anodes is necessary. The systems are inspected every three months. Anodes are weighed with a

spring balance (Figure 10) in order that their remaining life can be estimated and any necessary repairs are made to the systems.

For suspension, 7/16 inch cable is attached to an anode and this assembly is hung from the support bracket by means of a clevis and strain insulator (Figure 11). A length of No. 2 welding cable runs from a lug on the support cable to a junction box, inside of which is a 0.01 ohm shunt to aid in measuring the current output of the anode and an adjustable resistance for varying the output. At one time, junk sucker rods were used for suspending anodes, but supports of this type proved quite cumbersome.

b. *Cathodic Protection Checked.* In order to determine exactly how effective cathodic protection is for preventing corrosion of steel in sea water, two strings of weighed 5 x 5-inch steel plates were hung at 2-foot intervals from six feet above mean gulf level. These plates were fastened to 7/16-inch cable with ordinary wire line clamps. One of the test strings was insulated from the platform. The other was in electrical contact with the platform and maintained at approximately the same potential as the platform, at least 0.85 volts negative with respect to a saturated calomel electrode. At the end of one year, every third plate was removed from each string and evaluated. The corrosion rates of the plates as determined from weight loss are shown in Figure 12. Note that, contrary to what would be expected from an oxygen concentration standpoint, the corrosion rate on the unprotected string went up with increasing water depth. Red rust was found on the lower test plates of the unprotected string. The only plausible explanation for this phenomenon is that the protective film of marine growth decreases with depth. The protected string had an approximately constant rate of corrosion on the submerged portion of the string. A comparison of the two curves indicates that submerged steel in the Gulf can be almost completely protected by maintaining a steel-to-sea potential in the neighborhood of —0.85 volts. It should be emphasized that the corrosion rates on an unprotected platform may vary at different locations, depending on the electrical potential of strata through which casing is set.

The overall cost of cathodic protection for submerged steel runs between 5 and 8 cents per square foot per year. The current requirement varies but little whether the submerged portion of the platform is painted or is left bare, because steel is polarized rapidly in sea water.

3. Floating Equipment.

Although some operators build large self-contained platforms, most companies use smaller platforms in conjunction with drilling tenders. These barges, usually converted LST's or YF's, contain living quarters for crews, mud mixing facilities, mud storage, mud pumps, repair shops, laundry, fuel storage and distilling units for drinking water.

Much maintenance is required because of mechanical damage to coatings. Oil-modified alkyd coatings are used extensively on floating equipment for two reasons: they can be applied by unskilled men

Figure 10—Weighing magnesium anode to determine remaining life.
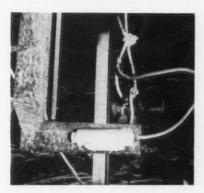
Figure 11—Anode suspension bracket showing junction box.
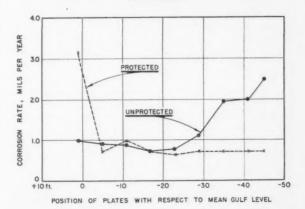
Figure 12—Effect of cathodic protection on weighed test plates which were submerged in the Gulf for one year.

POSITION OF PLATES WITH RESPECT TO MEAN GULF LEVEL

and they do not require the meticulous surface preparation of vinyls and epoxies. Although a sand blasted surface undoubtedly would greatly improve the performance of these materials, blasting cannot be done on deck in most cases because of the presence of unshielded machinery.
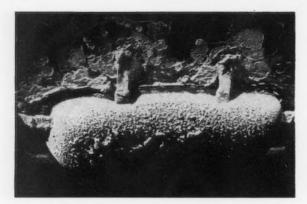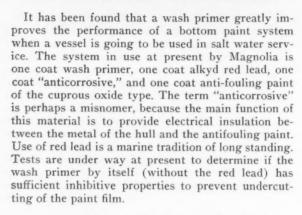
Figure 13—Slab-type magnesium anode on hull of a tug after three months in service. Note stripping of paint in vicinity of anode.

Figure 14—Bolted-type magnesium anode containing resistance washer for controlling current output of the anode.

It has been found that a wash primer greatly improves the performance of a bottom paint system when a vessel is going to be used in salt water service. The system in use at present by Magnolia is one coat wash primer, one coat alkyd red lead, one coat "anticorrosive," and one coat anti-fouling paint of the cuprous oxide type. The term "anticorrosive" is perhaps a misnomer, because the main function of this material is to provide electrical insulation between the metal of the hull and the antifouling paint. Use of red lead is a marine tradition of long standing. Tests are under way at present to determine if the wash primer by itself (without the red lead) has sufficient inhibitive properties to prevent undercutting of the paint film.

a. *Boats and Barges.* Cathodic protection also is applied to boats and barges. Figure 13 shows a slab-type magnesium anode welded to the hull of a tug. Figure 14 shows another type of magnesium anode designed for bolting to the hull. The current output of the latter type can be cut back for longer anode life by using special resistance washers when attaching the anodes to the hull. Figure 13 also shows what happens to an ordinary bottom paint in the vicinity of uncontrolled output anodes. The paint is destroyed for a distance of several feet around the anode. For this reason, the use of a patch of vinyl coating in the area is highly recommended. A coating which will stay in place near an anode assists in obtaining an adequate current distribution over the entire hull.

b. *Suspension System Tried.* In another instance, eight 100-pound magnesium anodes were suspended from bow and stern of one tender to see if a protective potential could be built up over the hull. The potential was approaching a protective value within a few days, but soon afterward a storm forced the barge to be brought in from the gulf, and half of the anodes were lost. One anode cable became entangled with a boat during rough weather. This design of a cathodic protection system for a drilling tender, while excellent for permitting renewal of anodes without drydocking the vessel and for providing good current distribu-

tion was considered a failure because it was not compatible with normal operations.

c. *Use of Welding Equipment.* Many drilling tenders have welding machines on them which are positively grounded to the barge hull. Frequently the negative lead will be taken to the platform and welding done there. When this is done without attaching an adequate return ground from the platform to the barge, the sea acts as a return for the welding current and the barge dissolves in the sea according to Faraday's law. This would amount to 0.7 pound of steel per hour when a 300 ampere machine is being used. Decomposition of a hull at this rate would be negligible if a hull were 100 percent bare steel. However it can result in serious pitting if only a small portion of the hull is bare, because all the dissolved steel will come from the bare areas. It is impossible for a few magnesium anodes to compete with a welding machine.

4. Conclusions.

The equipment necessary for offshore drilling and producing operations can be made to last as long as it is needed if the following procedures are followed:

1. Coat steel in the atmospheric zone of drilling and producing platforms with vinyl of at least 6 mils thickness.

2. Phenolics or alkyds are satisfactory for tankage and tank battery platforms in the atmospheric zone, although a vinyl system is preferred.

3. Have all coating done by a reputable applicator who has had experience with the type of material to be used.

4. There are many methods of protecting the splash zone. Choose the one which best fits the operating conditions. Expensive materials can be used in this zone without greatly increasing, percentagewise, the cost of the platform.

5. Cathodically protect all submerged surfaces.

6. Always run a heavy ground wire from platform to barge when welding.

Any discussions of this article not published above will appear in the December, 1955 issue.

Electrode Potentials*

By G. W. AKIMOV

Abstract

Characteristics of reversible and irreversible electrode potentials are defined with respect to the ionic patterns characteristic of the two states. Limits of ionic exchange are seen as significant in achievement of polarization by a metal surface. The theory of electrode potentials is considered at some length with pertinent mathematical derivations. Significance and characteristics of the double layer on a metal immersed in an electrolyte are reviewed with emphasis on ionic activity.

Theoretical and practical aspects of irreversible potentials are considered with respect to several metals and environments. Differences between the considerations affecting potentials of simple irreversible electrodes and complex electrodes are detailed in several liquid and gaseous environments. The effect of stress in lowering electrode potentials is covered, as are results of experiments in environments with oxidizers, chlorides and the effects of temperature, velocity of solution and time.
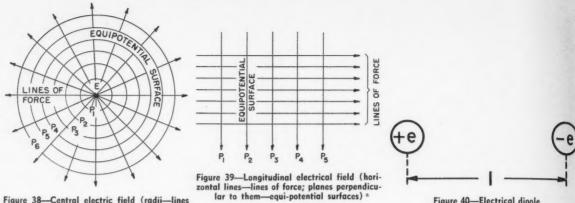
Potentials of active cathodes and anodes are discussed. Theoretical influence of films, current densities and direction and experiments with a copper-zinc couple are detailed. Uses of polarization diagrams are considered and the significance of anodic and cathodic control of a corroding system explained.

The author examines results of experiments with several complex alloys. The influence of the several components of the alloy is weighed and numerous cases involving different areas of cathode and anode and the difficulties involved in making experimental determinations of true potentials examined. Potentials of complex anodes of the film-pore type are determined by an experiment which includes a means of continuously cleaning the specimen of protective films. The nature and characteristics of films is covered as is the effect of varying thicknesses of film.

The effect of differences in lattice structure are investigated. Diagrams of potentials taken under varying conditions are given. 62 figures, 12 tables.

1. **Reversible and Irreversible Electrode Potentials.** Electrode potentials of a metallic surface immersed in an electrolyte are of importance in considering corrosion behavior. Three aspects of the problem will be considered here. First, we are interested in how the nature and magnitudes of the initial electrode potentials of different metals under different corrosion conditions are affected by varying factors. Second, it is important to know the distribution of original electrode potentials on metallic surfaces. In other words, we would like to know the magnitude of the electrode potential at every point of the metal-solution interface and thus be able to determine both the values of the original potential differences and the areas of the cathodic and anodic regions. Third, great importance is associated with variations of electrode potentials from the moment when the action of corrosion factors begins to be felt, i.e., from the time of immersion of the metal in an electrolyte, as a result of polarization phenomena and other secondary processes.

From the practical standpoint, we are interested in continuously acting currents generated in corrosion elements. These currents are determined by continuously existing potential differences. In other words, we are concerned with electrode potentials which have been modified already by the influence of polarization and other factors, because these very potentials define the strength of corrosion currents and ultimately the consumption of anodic areas, i.e., corrosion. However, the original potentials have a pronounced importance since they define the division of the metal-solution interface into anodic and cathodic regions and since the values of continuously operating potential differences are, to a certain extent, associated with the original electrode potentials.

Now one would like to know the nature of electrode potentials with which one deals in discussing corrosion processes. Electrochemistry is conventionally concerned with reversible electrode potentials.[3, 4, 5, 6, 8] These are equilibrium potentials between a metallic electrode and the ions of the same metal present in different concentrations in a corresponding solution, such as $Cu/Cu^+, Zn/Zn^{++}$, etc. These potentials follow the Nernst equation.

$$E = E_o + \frac{RT}{nF} \ln C_1$$

where C_1 is the concentration of metallic ions in the solution. In other words, the metal potential varies proportionally to the logarithm of its ion concentra-

tion in the solution. Strictly speaking, the concentration C_1 in the Nernst formula should be replaced with ionic activity under given conditions, particularly for moderately dilute solutions.

A perfectly definable state of labile equilibrium between a metal and a corresponding ion corresponds to every reversible electrode potential and can be expressed by a simple equation ($M \rightleftharpoons M^+$, for example $Cu \rightleftharpoons Cu^+$ or $Zn \rightleftharpoons Zn^{++}$, etc.) This means that an increase of ions of the metal in the solution surrounding an electrode will raise its electrode potential, while a decrease will correspondingly lower it, these changes being reversible. In this case, a definite value of an electrode potential corresponds to a given concentration (activity) of metallic ions in the solution. Electrode potentials of metals measured when the activity of ions in the solution is equal to unity are known as normal or standard potentials. It is evident that a comparison of electrode potentials of metals with each other has to be conducted under similar conditions, particularly using an identical

Figure 38—Central electric field (radii—lines of forces; spherical surfaces—equipotential surfaces)

Figure 39—Longitudinal electrical field (horizontal lines—lines of force; planes perpendicular to them—equi-potential surfaces) [a]

Figure 40—Electrical dipole.

activity of ions of the metals themselves in the solutions. As a rule, standard potentials are compared.

Recent investigations have demonstrated that there really exists a continuous interchange of ions between the metal and the solution. Ions pass from the surface of the metal into solution, while simultaneously the ions from the solution are transferred to the metal. This interchange of ions has been demonstrated by experiments employing "marked" atoms. When a radioactive isotope of a metal is introduced in a metallic electrode made of this metal, the isotope will be found, after a certain time, to be distributed between the two phases, namely between the metal and solution. A kinetic equilibrium between an electrode and a solution can exist only in case the velocity of ion migration from the metal into solution $M^+_s \rightarrow M^+_1$ is equal to the velocity of the opposing process $M^+_s \leftarrow M^+_1$.

Ion interchange between the two parts of this system has a pronounced practical interest, because the magnitude of this interchange, i.e., the velocity of the direct and the opposing processes, defines the stability of the potential.[14] It can be calculated, on the basis of certain electrical properties of the double layer at the interface metal-solution, that the potential becomes unstable when the velocity of the interchange is very low, less than 10^{-10} ampere/cm². Such a potential may be shifted by polarization to any new value, but the current created by the interchange of ions cannot restore it to the original magnitude within a finite time. Once the velocity of interchange is greater than 10^{-10} ampere/cm², the potential becomes stable. When such an electrode is polarized to any new potential and then the source of polarization is eliminated, the interchange current restores this potential to the original value within a finite time. The latter potential represents a kinetic equilibrium between the metal and its solution.

In the majority of corrosion processes one does not deal with solutions containing ions of a given metal, but with a solution containing foreign ions.[15] For example, one is liable to encounter an aluminum potential in 0.1N NaCl or a copper potential in 1N H_2SO_4 solutions, etc. At least at the beginning of the process the solution contains Na^+ ions in place of Al^{+++} ions and H^+ in place of Cu^{++}, etc. A problem is

raised here regarding which particular potentials are being measured and to which processes these potentials correspond. First, let us call irreversible electrode potentials those potentials for which the observations do not furnish direct evidence on the character of a reversible interchange process. These potentials extend very widely the realm of electrode potentials of metals, because for each metal we must consider not only potentials in solutions of its own ions, but also a multiplicity of potentials in solutions containing foreign ions. These latter potentials change as functions both of the cations and, frequently, of the anions present in the solution, and of their concentration. The simple Nernst formula deduced for equilibrium conditions is not directly applicable in the field of irreversible potentials. An application of the Nernst formula is possible only in the case where a reversible process can be found for an irreversible potential which, furthermore, assumes the stability of the potential.

2. Origin of Electrode Potentials. In any electrical field it is possible to find areas having an equal electrical potential. These areas are given the name of equipotential surfaces. These surfaces correspond to spherical surfaces in the case of a single-charge field, Figure 38. In a longitudinal field they are represented by planes perpendicular to the lines of force, Figure 39. The term of electric (or electrostatic) potential P is given to a force, the negative gradient of which is equal to the value of voltage tension E of the electrostatic field.[1]

$$E = -\,\mathrm{grad}\ P \qquad (13$$

The gradient of the potential is equal to a derivative of the potential along the perpendicular n to the equipotential surface,

$$\mathrm{grad}\ P = \frac{dP}{dn} \qquad (14$$

i.e., it presents the variations of the potential during motion in the field perpendicular to the equipotential surface, which corresponds to motion along the lines of force.

Let us assume that there are in an electric field two points, 1 and 2, which have different potential values P_1 and P_2. When a unitary electric charge (the value

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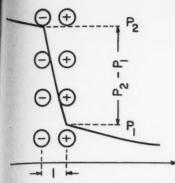
Figure 41—Schematic representation of a potential drop in a double layer.
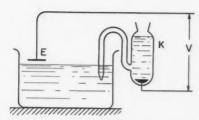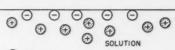
Figure 42—Measurement of a potential drop at the liquid-air interface.

Figure 43—Structure of a double layer at the KI liquid-air interface.
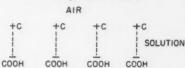
Figure 44—Structure of a double layer at the palmitic acid-air interface on the surface of an aqueous solution.

of the charge $e = 1$) is shifted from point 1 to point 2, a certain definite amount of work is exerted, this work being equal to

$$\int_2^1 dp = \int_2^1 E \, dn = P_2 - P_1 = A \qquad (15$$

In this expression, E is the voltage of the electric field and dn an element of path. A measure of potential with respect to any other potential can be, therefore, the work expended in the transfer of a unitary point charge.

In the future, we shall refer frequently to the concept of a double layer. Two electric charges having opposite signs, but equal values, placed at a definite distance from each other are called a dipole, Figure 40. The moment of a dipole is equal to the product of charge magnitude and the distance between the

$$u = e \cdot l \qquad (16$$

charges where e is the charge of dipole and 1 the distance between the charges. Many molecules form dipoles and have a definite dipole moment. The water molecule has a rather large dipole moment equal to 185×10^{-18} electrostatic units. The positive end of the molecule consists of two hydrogen ions and the negative end of an oxygen ion. Molecules of many organic compounds also have large dipole moments.

A double layer may be conceived as a very thin layer composed of dipoles. The thickness of the layer is defined by the distance between the charges of the dipoles composing the double layer. Dipole density (D) in a double layer corresponds to the number of dipoles per square centimeter of the layer surface. The energy (T) or moment of a double layer can be expressed, similarly to the moment of a single dipole, as the product of layer density and the thickness of the layer (l)

$$T = Dl \qquad (17$$

It has been shown in electrostatics[2] (Green theorem) that on passing from one side of a double layer to the opposite a change of potential takes place, the magnitude of which is expressed by the difference of potentials.

$$P_2 - P_1 = 4 \pi T = 4 \pi Dl \qquad (18$$

Thus, a greater density of dipoles in a double layer and a greater distance between the charges leads to a larger potential change in a double layer. Figure 41
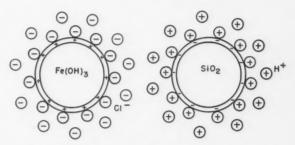
Figure 45—(Left) Colloidal particle of Fe(OH)₃ showing adsorbed chloride ions.
Figure 46—(Right) Colloidal particles of SiO₂ showing adsorbed hydrogen ions.

presents schematically the structure of a double layer and the change of potential on passing through a double layer.

At the interface of two phases one meets with a double layer and with a corresponding potential.[8, 9] Let us examine, for example, the air-solution interface, Figure 42. The potential at this interface can be measured by means of a disc electrode E and a calomel electrode K by placing certain substances, for example, oil on the surface of the solution or by introduction of different electrolytes into the solution. In order to conduct the measurements, the surface of the flat electrode E is coated with a thin layer of a radioactive substance. This causes the air gap between the electrode and the solution to become conductive due to a certain amount of ionization of the air. When 0.01N aqueous HCl is used as the solution and a solution of myristic acid is placed on it, the potential exceeds 200 mv. Introduction of KI into the solution also results in a potential of the air-solution interface. In the latter case, the surface absorbs principally negatively charged ions of iodine and forms a double layer, as shown in Figure 43. A layer of palmitic acid on the surface of an aqueous solution produces a double layer with a different distribution of the charges, because the chains of palmitic acid arrange themselves at the surface so that the positive end of the molecule (hydrocarbon) is found on the surface and the negative (hydroxyl) in the solution, Figure 44. Double layers of this nature and potentials

Figure 47—(Left) Double layer formed when metallic ions leave the metal and enter the solution.

Figure 48—(Right) Double layer formed when anion from the solution is adsorbed on the metal.

corresponding to this may be given the name of adsorptive layers and potentials in view of the mechanism of their formation. The phenomenon of ionic adsorption on colloidal particles must also be associated with the formation of double layers. A colloidal particle of $Fe(OH)_3$ in a solution containing chloride ions is charged positively on the surface and attracts negative chloride ions, Figure 45, while a particle of SiO_2 adsorbs positive hydrogen ions in an acid solution, Figure 46.

The presence of different phases creates pronounced difficulties in determining the potential of a double layer. In this measurement, one has to deal with a series of potentials and must use the result of determinations of this total in place of a single value. However, it is possible to determine variations in the potential under certain changes in conditions of the system. The above mentioned example of measuring the potential at the air-solution interface, Figure 42, leads one to consider at least four potentials in different double layers, namely:

1) solution-air,
2) air-flat electrode,
3) flat electrode-calomel half cell K and
4) calomel half cell-solution.

It is evident that the results of the measurement cannot be connected with any definite electrode potentials. When, however, we add KI to the solution and measure the potential, this measurement may be correctly referred to the solution-air interface,[1] since any changes at the calomel half cell-solution interface produced by the addition of potassium iodide can be determined and calculated beforehand.

A characteristic property of all double layers is a relative immobility of the charges of the double layers, because they are supported on a dielectric. A detailed study of double layers of this type has shown that its structure is more complex. Behind the immobile charges of the outside layer there is in the solution a thicker layer of relatively mobile ions, the so-called diffusion layer of Jug-Stern.[13]

Let us examine now the origin of a double layer on a metal immersed in an electrolyte. Three modifica-

tions are possible here. First, hydration forces occurring between the metal and the electrolyte might be greater than the bonds between ions and electrons in the metal. In this case, a certain number of ions will leave the surface of the metal and enter the solution as hydrated ions. These ions form the outside or positive portion of the double layer, while the inside portion will be formed by an equivalent amoun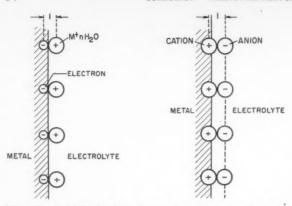t of residual electrons remaining in the metal. It should be emphasized that ions entering the solution cannot leave the surface of the metal on account of electrostatic interaction (attraction) between heteropolar portions of the double layer, i.e., between electrons and hydrated ions. As a rule, only a small proportion of the surface ions enter the solution, because only a comparatively low charge density at the interface metal-electrolyte creates a considerable potential difference. Once a double layer is formed by the passage of a certain number of ions into solution, the passage of new ions into the solution becomes more difficult in proportion to the interaction between the two surfaces of the layer until the fission between ions and electron becomes impossible. Figure 47 presents a double layer of this type; here the metal is charged negatively and the solution positively. Double layers of this type are produced on immersing many electronegative metals (Zn, Cd, Mg, Fe, etc.) into water, or solutions of acids, alkalis and salts.

When the power of hydration is not sufficient to sever the bond between an ion and an electron, a double layer of a different type may be created. A certain number of cations present in solution may be adsorbed on the surface of the metal forming a positive inside film of the layer, while the outside film will be made up of the excess anions of the solution attracted to the surface of the double layer by electrostatic action. The arrangement of the outside films of the double layer is, therefore, opposite to the one recorded in the previous case. In this case, the metal is positively charged, while the solution carries a negative charge, Figure 48. Double layers of this type occur, apparently, on more electro-positive metals on their immersion in solutions having a high concentration of cations of electro-positive metals, such as platinum in a solution containing Pt^{++} or gold, or silver or mercury in a solution of mercury salts, etc.

Finally, sometimes it happens that neither are metallic ions able to leave the metal and pass into solution, nor are cations of the solution able to be adsorbed on the metal. In this case, there is no possibility of double layer formation as a result of an electrode process. However, there is a chance in this case of building a double layer as a result of different processes, for example, by adsorption of gases dissolved in the electrolyte. Let us assume that platinum is immersed in a neutral solution. Platinum ions do not enter this solution; at the same time the solution lacks a sufficient quantity of positive ions which could adsorb on the metal. The solution contains, however, a few molecules of dissolved oxygen. The

latter are adsorbed on the surface of platinum, forming first atoms and then ions,

$$0_2 \rightarrow 20$$
$$20 + 4e = 20^{--}$$

so that a double layer is produced which has an outside film composed of oxygen ions and the inside one consisting of positively charged platinum ions. With a low oxygen concentration in the solution, this potential probably will be unstable.

Passing oxygen through the solution produces an equilibrium between oxygen ions on the surface of metal and OH^- ions in the solution, so that a platinum electrode will behave like a stable oxygen electrode.

$$O^{--} + H_2O \rightleftharpoons 20H^-$$

The mechanism of double layer formation at the metal-electrolyte interface is actually much more complicated than the schematic representation given above. The structure of double layers is, probably, more complex than the system of two simple homogenous outside films. Under certain conditions, for example, in very dilute solutions, there are possibilities of a diffusion zone existing in a metal directly behind the "rigid" outside film on the surface of metal. In some cases, double layers are very complex. A considerable portion, probably even a major portion, of ions of the metal itself are replaced in the outside film with other cations present in the solution. A further complication in the structure of double layers may be produced by other atoms and molecules either adsorbed on the metal before it is immersed in an electrolyte or deposited on the surface of the metal from the electrolyte. As will be shown later, a particularly important part is played by gases, principally oxygen present in air and dissolved in practically all electrolytes.

Two characteristic properties of double layers on metals should be noted: first, the outside films of the double layer are present in different phases, in a liquid and on a solid; second, an interchange of electrons between the metal and the solution is possible here under certain conditions because the inner conducting film contains either excess electrons (negative charge) or, inversely, lacks electrons (positive charge).

3. **Irreversible Potentials of Electrodes.** Before starting a discussion of irreversible potentials of metals in solutions of foreign ions, some remarks are in order regarding potentials of metals in solutions of their own ions. Such potentials are generally considered to be reversible. Many metals, for example mercury, copper, silver, and cadmium, show sufficient agreement with the Nernst equation over a wide range of solution concentrations of their own ions. There is, however, a group of metals for which the Nernst equation is not applicable at all.[10] To this group belongs such a technically important metal as iron. Potentials of aluminum and magnesium in solutions of their own ions also do not obey the Nernst law. Furthermore, certain metals, which in general follow the Nernst equation, cease to do so when the concentration of their own ions is very low. The relation between the potential of cadmium and the degree of
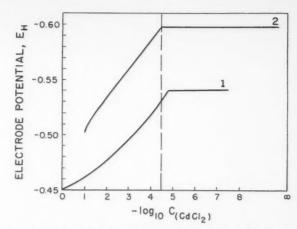
Figure 49—Changes of Cd potential in a $CdCl_2 + CdSO_4$ solution (Curve 1) and in a 1 N KCl + $CdCl_2$ solution (Curve 2) as a function of cadmium salt concentration (Gatty and Spooner).

TABLE 6—Electrode Potentials of Metals in 3% NaCl and 3% NaCl + 0.1% H_2O_2 Solutions (Hydrogen Scale) (Akimov)

Metal	Electrode Potential in a 3% NaCl Solution		Electrode Potential in a 3 + NaCl +0.1 H_2O_2 Solution		Standard Potential
	Original	Final	Original	Final	
		VOLTS			
Ag	+0.24	+0.20	+0.23	+0.23	+0.80
Cu	+0.02	+0.05	+0.20	+0.05	+0.34
Bi	−0.15	−0.18	......	......	+0.28
Sb	−0.12	−0.09	......	......	+0.25
Sn	−0.25	−0.25	−0.08	+0.1	−0.1
Pb	−0.39	−0.26	−0.35	−0.24	−0.12
Ni	−0.13	−0.02	+0.2	+0.05	−0.22
Co	−0.17	−0.45	......	......	−0.29
Cd	−0.58	−0.52	+0.50	−0.50	−0.40
Fe	−0.34	−0.50	−0.25	−0.50	−0.43
Cr	−0.02	+0.23	+0.40	+0.60	−0.557
Zn	−0.83	−0.83	−0.77	−0.77	−0.76
Mn	−1.05	−0.91	......	......	−1.04
Al	−0.63	−0.63	−0.52	−0.52	−1.34
Mg	−1.45	......	−1.4	......	−1.55

dilution is shown, for example, in Figure 49. Down to a concentration of $10^{-4.4}$ N the potential varies with the logarithm of concentration and follows the Nernst equation, though not exactly. Below this concentration, the cadmium potential does not depend on concentration. The causes of this phenomenon are not fully understood as yet, but some probable hypotheses may be offered. According to one of them, the independence of potential from concentration after a certain lower limit has been passed can be explained by the metal generating a certain minimum quantity of its own ions even when immersed in pure water. Thus, we cannot reduce the actual concentration of metallic ions at the metal surface beyond a certain limit by lowering the ion concentration in a solution. Another explanation consists in considering that the ions of a metal when present in a very low concentration are incapable of participating in the formation of a double layer so that double layers of a second type are formed, involving the participation of the OH^- ions of water.

It can be seen, therefore, that the potentials of metals in solutions of their own ions do not seem to be reversible for all metals and for all conditions.

A study shows that the nature of irreversible potentials in solutions of foreign ions is not always the

Figure 50—Changes of the potential of copper as a function of NaCl concentration (Akimov and Batrakov).

TABLE 7—Electrode Potentials of Metals in 1 N Solutions of KCl, KOH, and HCl Saturated with O₂, H₂ and N₂ Given on Hydrogen Scale in Volts (According to Kreiger and Kahlenberg).

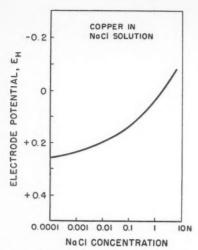| Metal	Gas O₂			Gas H₂			Gas N₂		
	KCl	KOH	HCl	KCl	KOH	HCl	KCl	KOH	HCl
Ag	+0.186	+0.10	+0.202	+0.185	−0.070	+0.205	+0.193	+0.090	+0.210
Al	−0.53	.....	.....	−0.525	.....	.....	−0.535	.....	.....
Au	+0.415	+0.440	+0.780	+0.430	+0.050	+0.690	+0.420	+0.080	+0.780
Bi	+0.034	−0.272	+0.100	−0.050	−0.390	+0.075	−0.030	−0.375	+0.090
Cd	−0.50	−0.980	−0.565	−0.575	−1.007	−0.575	−0.570	−0.980	−0.575
Co	−0.170	−0.55	−0.10	−0.315	−0.610	−0.167	−0.310	−0.590	−0.160
Cr	+0.38	−0.310	.....	+0.260	−0.800	.....	+0.240	−0.770	.....
Cu	+0.035	−0.035	+0.240	−0.025	−0.305	−0.030	−0.015	−0.300	−0.030
Fe	−0.495	−0.270	−0.29	−0.475	−0.675	−0.340	−0.455	−0.670	−0.350
Hg	+0.255	+0.096	+0.26	+0.244	+0.056	+0.270	+0.244	+0.065	+0.265
Mg	.....	−0.890	.....	.....	−1.180	.....	.....	−1.145	.....
Mo	+0.080	−0.320	+0.395	+0.050	−0.400	+0.376	+0.034	−0.415	+0.365
Ni	−0.020	+0.052	−0.070	−0.420	−0.095	−0.125	−0.115	−0.040	−0.125
Pb	−0.265	−0.555	−0.290	−0.320	−0.600	−0.315	−0.302	−0.610	−0.315
Pt	+0.425	+0.130	+0.720	−0.250	−0.540	+0.030	+0.380	+0.100	+0.650
Sb	−0.075	−0.554	+0.170	−0.185	−0.610	+0.112	−0.173	−0.620	−0.115
Si	+0.025	−0.375	−0.170	−0.088	−0.282	−0.260	−0.120	−0.310	−0.220
Sn	−0.220	−0.560	−0.307	−0.260	−0.770	−0.330	−0.250	−0.760	−0.320
W	+0.005	−0.370	+0.340	−0.037	−0.420	+0.345	−0.028	−0.420	+0.305
Zn	−0.830	−1.234	−1.225	−0.840	−1.245	−0.835	−1.245	−1.240	−1.240

same and that in the realm of corrosion one has to deal with several typical cases of irreversible potentials of different character. Table 6 gives the values of electrode potentials for most of the important metals, determined in 3% NaCl and in 3% NaCl + 0.1% H₂O₂ solutions.

Let us suppose that the electrode potential of zinc in a 1 N solution of KC1 is being measured. This potential stabilizes comparatively rapidly and its value is around −0.85 volt. A comparison of this value with the reversible normal potential (−0.76 V.) indicates that they are comparatively close together. The value of −0.85 V really would correspond to the reversible potential of zinc in a solution of its own ions at a concentration of the latter equal to 0.01 — 0.001 N. Since zinc is a strongly negative metal, it is quite probable that the immersion of zinc in any electrolyte, or even in pure water, would cause a certain number of zinc ions to pass instantaneously into solution forming a double layer of the type e (metal)—Zn⁺⁺ (solution). In the presence of oxygen, an imperfect surface of zinc forms microcouples and the action of these microcouples causes a certain amount of zinc ions to go into the solution. In this case, the nature of the double layer and of the electrode potential is similar to that for the conventional equilibrium potential of zinc, with the difference that the structure of the double layer is, probably, more complex on account of many foreign ions being present in the electrolyte. Since the potential of zinc changes but slightly with the concentration of its own ions, a certain increase or decrease in concentration of zinc ions in the solution at the surface of metal, associated for example with a different number of microcouples (cleaner or dirtier metal), has but a slight effect on the magnitude of the electrode potential. Certain irreversible potentials may be considered, therefore, as distorted reversible potentials of the first type.

Let us assume that we have a copper electrode immersed in a 1 N solution of NaCl. Experimental data indicate that the electrode potential of such an electrode is + 0.05 v. When this value is compared with the potential of a reversible copper electrode at a low concentration of copper ions (of the order of 0.001-0.00001 N) it appears that the irreversible potential is much more negative. On this basis, it is entirely impossible to consider this potential as a variation of a common reversible potential of the first type. However, in studying many irreversible potentials there is another way of approaching the subject. Certain metallic electrodes in solutions of foreign ions behave as electrodes of the second type, which are reversible with respect to anions, for example electrodes frequently used in electrochemistry such as $Hg/Hg_2Cl_2/Cl^-$, $Ag/Ag\ Br/Br^-$, $Cu/Cu_2O/OH^-$, etc.

As is well known, for these electrodes the concentration of their own ions and a corresponding value of the electrode potential can be expressed as a solubility product. For example, for an electrode $Cu/CuCl/Cl^-$ this solubility is $[Cu^+] [Cl^-] = Const. = 1.7 \times 10^{-6}$. (Brackets are used to indicate concentrations of cations and anions.)

Increasing the chloride-ion concentration reduces the electrode potential. With the decrease of chloride-ion concentration the concentration of Cu^+ ion increases proportionally and, correspondingly, the potential of the electrode also increases.

Figure 50 presents a relation between the potential of copper in a solution as a function of the logarithm of the chloride concentration.[18] While a straight line relation is lacking here, it is clear that the increase in chloride-ion concentration leads to a drop in copper potential, which was to be expected assuming that we are concerned here with a system corresponding to an electrode of the second type $Cu/CuCl/Cl^-$. This potential does not, of course, correspond completely to the equilibrium potential, because the present conditions are more complicated. Certain distortions arise here on account both of the electrode failing to reach an instantaneous equilibrium with the solution and on account of certain complicating phenomena. In particular, the conditions employed render possible the formation of complexes reducing the concentration of the ions of the metal proper at the electrode.

It can be admitted, therefore, that some irreversible potentials are really distorted reversible poten-

tials of the second type. Immersion of a copper plate into a solution containing OH^- ions produces an electrode of the second type which is close to a $Cu/Cu_2O/OH^-$ electrode. The value of this potential is defined basically by the concentration of the OH^- ions. Many other metals, particularly the electropositive ones, also form electrodes of the second type in solutions of foreign ions, provided the reaction products between the metal and the electrolyte have a comparatively low solubility product.

While electrode potentials of electrodes of the first type composed of pure metals may be used to some extent as a rough measure of their corrosion characteristics, the potentials of electrodes belonging to the second type do not have any simple relation to the corrosion behavior of the metals. Let us examine copper in a 0.1 N solution of NaCl and in a 0.1 N solution of NaOH. In the 0.1 N solution of NaCl, the potential of copper is —0.13 v and in a 0.1 N solution of NaOH it is +0.05 v. At the same time, copper corrodes much faster in a chloride solution than in a solution of alkali.

4. **Factors Affecting Electrode Potentials.** In the realm of corrosion one meets most frequently with initial electrode potentials of the following types:

  A. Potentials of simple irreversible electrodes.
    1. Reducible to reversible electrodes of the first type.
    2. Reducible to reversible electrodes of the second type.
  B. Potentials of complex electrodes.
    1. Having a binary or more complex structure.
    2. Potentials of the film-pore type of electrodes.
    3. Potentials of solid solutions and intermetallic compounds.

We very seldom have to deal with potentials of gas electrodes, such as hydrogen, oxygen, or chlorine, as initial electrode potentials. However, as we shall see later, the potential of a working cathode may be considered in a majority of cases as the potential of an oxygen or a hydrogen electrode.

The phenomena of electrode potentials relate to the boundary region between a metal and a solution. We can separate the initial factors, therefore, from the numerous other factors affecting the magnitude of an electrode potential.

  1. Internal factors associated with the metal itself, namely its nature, physico-chemical state and structure, the state of its surface, the presence on the metal of protective films (initial ones), atoms and molecules adsorbed on the surface, mechanical deformations and stresses in the metal.
  2. Outside factors associated with the electrolyte such as the chemical nature of the solvent, nature and concentration of ions in the solution, nature and concentration of dissolved gases and other substances which do not dissociate into ions. In the same group can be included factors related to the physical conditions such as temperature, pressure, light, etc.

Finally, we can combine with the initial factors all factors originating in the process of corrosion itself as a result of varying secondary reactions. To this class belong secondary protecting films and layers of corrosion products which also can have an effect on the magnitude of the electrode potential. There is no detailed investigation available until now bearing on the influence of different factors on irreversible electrode potentials. On this account, we are in a position merely to estimate the sequence of action of this or that factor and to determine the influence of but a few important ones. It is evident that the same factor might exert an entirely different effect depending on the character of the electrode potential, which might belong to the first or second type, or be represented by a complex electrode, etc. The influence of any given factor is particularly difficult to establish without a specific investigation in the case of complex electrodes. There is no doubt that the nature of the metal used is of greatest importance among the factors having an influence on the electrode potentials. On passing from one metal to another using the same solution under identical conditions, the electrode potential may vary from —3.0 v for lithium to +1.0 v for platinum, i.e., within the range of about 4 volts.

The state of the surface, namely greater or less uniformity of mechanical treatment, its cleanliness, etc. can affect the electrode potential appreciably (by about 1 volt). A particularly pronounced effect is caused by the initial protecting films. In this case, one has to deal mostly with complex electrodes of the film-pore type. Protecting films can change the value of electrode potentials in certain cases, and the changes involved may reach 1 volt or more. As a rule, protective films raise the potential of the metal. Conversely, the destruction of primary films in solution, an increase of number and size of pores and cracks, as well as an increase of permeability of these films to ions of the solution are, in general, associated with lowering of the electrode potentials. A strong action is exerted on certain metals by the atoms of gas dissolved in the liquid and adsorbed on the metallic surface, or of a gas in which the metal was held before immersion in the electrolyte.

Thus, for example, the potential of copper in a 1 N solution of KOH is equal to about —0.35 v in the presence of oxygen and to —0.305 v when oxygen is replaced with hydrogen; for tin in a 1 N solution of KCl the potential becomes equal to —0.22 v in the presence of oxygen and to —0.26 v in the presence of hydrogen. Additional information bearing on the effect of gases adsorbed on the surface can be found in Table 7.

For the most part, electrode potentials of metals in the presence of oxygen are more positive than in the presence of hydrogen. This holds valid for practically all metals and for all solutions with a few exceptions, as can be seen from a comparison of potentials of different metals in different electrolytes in the presence of oxygen or of hydrogen (Table 7). This effect of gases adsorbed on the surface of metals on their potentials may be explained in the following manner. Oxygen, while being adsorbed on the metal, forms at least partially negatively charged ions. Electrons at the surface of the metal are repelled from the negatively charged ions and move farther away from the surface, which results in a greater energy consumption for the escape of the electrons and a correspondingly increasing electrode potential. On the other hand, hydrogen atoms adsorbed on the surface form positive ions. An interaction among positive hydrogen ions and electrons facilitates the reac-

Figure 51—Schematic representation of double layer produced by adsorption of hydrogen and oxygen on metal.

tion of separating the metallic ion from electrons, i.e., reduces the energy of ion escape. As a result of this, the electrode potential becomes more negative. It is possible also to conceive the formation of double layers during the adsorption of both oxygen and nitrogen on the surface of the metal. In the case of oxygen adsorption and formation of negatively charged O^{--} ions, a positive charge is created at the metallic surface; conversely, adsorption of hydrogen and the formation of positively charged H^+ ions causes the metal itself to become positively charged. There is no need in this instance for all adsorbed atoms to pass into the ionic state. It is sufficient that only a small portion of the metallic surface carries either oxygen or hydrogen ions. Double layers associated with adsorption of oxygen or hydrogen on a metal are shown in Figure 51 (*a* and *b*).

Other gases, for example nitrogen, also have an effect on electrode potential, but the mechanism of their reaction is still completely unknown. The order of influence of adsorbed gases on electrode potentials may be estimated as hundredths or some times as tenths of a volt. Other atoms and molecules adsorbed on metal most probably have an effect on electrode potential, but until now, we have too few experimental data to elaborate on this point.

Deformation and stresses in metals usually lower electrode potentials, although, in a majority of cases but slightly, by thousandths or hundredths of a volt. The influence of these factors may depend on two different causes:

First, a deformed metal has, apparently, a somewhat lower energy of escape, because in this case a metallic ion is more free to leave its space lattice; in other words, the metallic bond can be broken more easily in this case.

Second, when a metal forms an initial protecting film or this film is produced at the first moment of electrolyte action, such a film on a deformed or stressed metal is weaker and can be more easily destroyed under the influence of internal stresses in the metal. On this account, a protecting film on a stressed metal contains, in general, more fissures while these fissures are probably of larger dimensions than those present in a film covering a metal free from internal stresses and deformations.

Figure 52 presents the influence of stresses on the electrode potential of brass in a 1 N NaCl + 1% HCl solution, while Figure 53 gives the changes of potential of duralumin in the same solution. In both cases, stresses are expressed as percentage of the proportional limit of the metal. From the above data it can be seen that stresses varying from zero to the proportional limit lower the electrode potential by several tenths of a millivolt.

From among the external factors, we shall concentrate our attention first on a very important property of the electrolyte, namely, on the hydrogen ion concentration.

Even a cursory examination of data given in Table 7 shows that variations in pH of the solution, exemplified by typical normal solutions of KOH, KCl, HCl, have a pronounced influence on the magnitude of the electrode potential; the order of variations involved is defined by tenths of a volt in a range of roughly 1 volt. Different metals show a different response to variations of the pH.

A pronounced effect on the electrode potential is exerted by the presence of oxidizers in a solution. Oxygen dissolved in the electrolyte most frequently acts as an oxidizer in corrosion processes. As a rule, oxidizers increase the electrode potential. Besides the influence of adsorbed oxygen, an increase in electrode potential may also be associated with the formation of an oxidic protecting film or with the reduction of pores and fissures in the original film. In general, oxidizers aid in the formation of a good protecting ox-

TABLE 8—Comparative Penetrating Power of Anions (Evans and Britton)

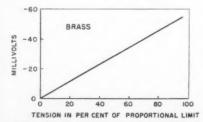| Salt	Current Density a/cm2
KCl	3.9
KB2	3.5
KI	2.9
KF	0.8
K2SO4	0.14
K3VO3	0.03
K3PO4	0.003

Figure 52—Changes in electrode potential of brass as a function of tension up to proportional limit. 1 N NaCl + 1% HCl solution. (Krenig and Bulycheva).
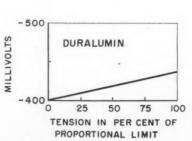

Figure 53—Changes in electrode potential of duralumin as a function of tension up to proportional limit. 1 N NaCl + 1% HCl solution. (Krenig and Bulycheva)
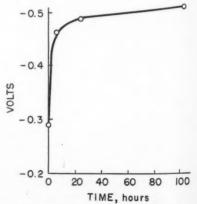

Figure 54—Changes of electrode potential of iron in a 3% NaCl solution in the presence of air (Akimov).

idic layer on the metallic surface. In this case, an increase of potential is associated with a lowered corrosion velocity.

Even when an addition of an oxidizer has but little effect on the condition of the film, this addition may still cause an appreciable increase of the electrode potential in the case of complex electrodes. The presence of an oxidizer might lower cathodic polarization which leads to an increased cathodic potential so that the total measurable potential also becomes more electropositive. Such an influence of an oxidizer might not be accompanied with decreased corrosion velocity. On the contrary, in such cases quite an intensive corrosion might take place simultaneously with an appreciable increase of the potential. The potential of copper in a 2 N solution of nitric acid is, for example, $+0.277$ v after 24 hours, at which time an intensive attack on copper is taking place with the evolution of nitrogen oxides; in a 2 N solution of sulfuric acid the potential after 24 hours is more negative and is qual to $+0.1978$ v but the corrosion velocity of copper in this solution is quite low.

Sharp changes of the potential towards positive values are frequently related to the passing of the metal into the passive state, in which a metal ceases to be active in respect to a given medium and behaves substantially as a noble metal. Passivity frequently occurs when a given concentration of an oxidizer is reached in the solution.

In a study of the influence of pH and of oxidizers on electrode potentials, it is very important to have systematic results of an investigation for a given moment in place of scattered data. Up to the present time only a very few E_M — pH diagrams have been constructed.

A pronounced influence on the electrode potential is also exerted by the complex formers because they reduce the concentration of metallic ions at the surface of the metal by combining ions of the metal which have passed in solution into stable complexes and therefore greatly reduce the corresponding potential.

Copper in cyanide and ammonia solutions can have, therefore, a very low electrode potential; in an 1 N solution of NH_4OH, copper has, for example, a potential of -0.226 v after one hour. Gold, copper and mercury have low values of potentials in cyanide solutions for the same reason. A higher concentration of a complex former is usually associated with lower values of electrode potentials.

When a metal is coated with a protecting film which leads to change of its potential, a perceptible, (and occasionally pronounced) lowering of this potential may be produced by ions which can easily penetrate through the protecting film. The first rank among these ions is occupied by Cl^- ions; ions of SO_4^{--}, NO_3^- etc., have a much lower penetrating power.

Certain information bearing on the penetrating power of ions can be obtained by measuring the current between an aluminum anode and a platinum cathode immersed in a solution containing 0.001 mole of potassium chromate and a salt of the metal under investigation (0.05 mole). The presence of chromate is necessary to assure continuous restoration of the protecting film on aluminum. Since aluminum oxide is an insulator, the measured current strength depends on the penetrating property of the anions. A greater current strength corresponds to a greater penetrating power of anions. These measurements are conducted under standard conditions.

Data bearing on the penetrating power of different ions are tabulated in Table 8.

Potentials of metals coated with a protecting film immersed in the chloride-containing solutions frequently change gradually and not instantaneously, since a certain time is required for the penetration of chloride ions through fissures and pores in the film to the metallic surface. While oxygen atoms in general are capable of maintaining a protective film on many metals, chloride ions tend to destroy the protective film on many metals, so that in this respect oxygen and chloride ions are antagonistic. In Figure 54 an example is given of the effect of chloride ions on the potential of a metal already coated with a protective film by exposure to the air. It can be seen that, in the course of time, chloride ions penetrate through the protective film in spite of oxygen being present in the solution. This results in a pronounced lowering of the electrode potential. A particularly sharp potential drop takes place when chloride ions destroy the passive state of a metal. In this case, even a low concentration of chloride ions may lead to a large drop of the potential. For example, 18-8 stainless steel can be readily passivated in a weak solution of $KMnO_4$, resulting in a positive potential of about $+0.65$ v. This state is not stable, however, because one need only add some hydrochloric acid to the solution to cause the potential to drop to much more negative values, close to $+0.1$ v. At this point a strong corrosion process starts, so that this value of the potential is associated with a complex and effectively working electrode, Figure 55.

The influence of such factors as temperature, pressure, light, etc. on irreversible electrode potentials has not been studied to any appreciable extent. Usually the influence of temperature does not exceed some hundredth parts of a volt for each 10 degrees. The changes of temperature may be associated, however, with changes of other more effective factors, for example, oxygen concentration in the solution, so that the effect of the temperature factor might become much stronger.

In the realm of corrosion, the motion of a solution constitutes an important factor. This factor can change the potential either in the positive or in the negative direction depending on the nature of the metal and the conditions of the surrounding media. A lowering of potential connected with the motion of the solution is frequently associated with a lowering in the concentration of the metallic ions at the metallic surface. Ions which had passed into solution can be more easily removed from the surface by motion of the solution than by diffusion and convection currents alone. Occasionally, a drop of potential might be associated with a more rapid supply to the metal surface of substances which can form insoluble compounds and complexes with ions of the metal. An increased potential observed during motion of the so-
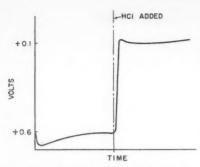
Figure 55—Changes in electrode potential of 18% Cr-8% Ni stainless steel in a 0.005% KMnO₄ passivating solution on adding 1 cc of activating HCl. Solution volume was 75 cc and the surface of specimen 6 square centimeters Akimov and Vzutserick).
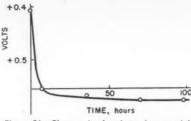
Figure 56—Changes in the electrode potential of chromium in a 3% NaCl + 0.19 H₂O₂ as a function of time (Akimov).
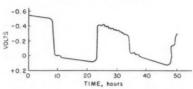
Figure 57—Changes in the electrode potential of iron in a 1 N solution of KNO₃ (Gatty and Spooner).

Figure 58—Changes in the electrode potential in a 1 N solution of K₂SO₄ of the 18% Cr-10% Ni-0.04% C alloy quenched from 1100° C (Strauss).

lution usually takes place either when the solution contains substances furthering the development of a passive state (frequently oxygen), or, in the case of complex electrodes, when stirring strongly reduces cathodic polarization through a more effective supply of depolarizer to cathodic areas.

The influence of factors originating in the process of corrosion proper is very specific and depends to a great extent on the corrosion process taking place.

For a clearer comparison of the effect of the above mentioned factors on change of potential, the following tabulation may be helpful.

Chemical nature of a metal	Whole volts (up to 4 volts)
Surface state (including primary protecting film)	Tenths of a volt
Adsorbed atoms and molecules on the surface (principally O₂ and H₂ molecules)	Hundredths and tenths of a volt
Mechanical deformation and stresses	Thousandths and hundredths of a volt
Chemical nature and concentration of the solution	Tenths and whole volts
Temperature (for each 10° C)	Hundredths of a volt

Quite frequently irreversible electrode potentials vary with time. Occasionally the change of potential takes place during many hours. In other cases it reaches its final value comparatively rapidly, often in

a few minutes or within 1 to 2 hours. Potential changes with the time may be affected by very different causes: Secondary processes associated with the formation of a protective film or strengthening of the films already present, processes of decomposition of protecting films, processes of gas adsorption from the solution or adsorption of any other substances, reaching an equilibrium associated with the saturation of the solution with reaction products between the metal and the electrolyte, polarization processes occurring on microelectrodes of complex electrodes, etc. A typical curve, given in Figure 54, presents the changes of potential in negative direction caused by the destruction of a protecting film; the curve given in Figure 56 shows an increase of the potential of chromium caused by the repair of the protective film by the action of oxygen present in the solution and despite the presence of chloride ions. In some instances the curves presenting the changes of potential with time have a complex shape, as shown in Figure 57. It is difficult, as a rule, to find an adequate explanation of such behavior of the curve without a special investigation. When the conditions are such that the metal is on the borderline between the passive and active states, periodic changes of the potential in the course of time may be frequently associated with spontaneous periodic passivation and activation of the metallic sample. These conditions vary not only the amplitude of the potential changes, but also the period of oscillations. Figure 58 gives an example of such a curve.

End of Part 1

Part 2 will be published in December, 1955 issue.

Three Papers on

SULFIDE CORROSION

Editor's Note: The complexity of the sulfide corrosion problem allows
for many avenues of approach and a variety of results. Reports on three
investigations are printed in this issue to stimulate work on the problem.

A Note on the Value of Ammonia Treatment For Tank and Casing Annulus Corrosion By Hydrogen Sulfide*

By WALTER F. ROGERS

Introduction

IN OCTOBER, 1949, Gardner et al[1] presented data showing that the injection of anhydrous ammonia into the vapor space of tankage handling sour crude oil successfully reduced the corrosion rate of the tank steel. As a result of this disclosure tests were started in February, 1950, in a Gulf tank at Wink, Texas, to determine the value of such treatment for pipe line tanks handling West Texas-New Mexico oils. Since that date ammonia treatment has been extended to a total of 13 pipe line tanks varying in size from 55,000 to 80,000 barrels capacity.

The amount of anhydrous ammonia injected per day has varied from 8 to 18 pounds. The rate of corrosion resulting from this treatment has been followed carefully through the use of coupons and a study of the history of the tank decks. Considerable laboratory data also have been accumulated on the mechanism of hydrogen sulfide corrosion of steel[2] and it is now possible to draw rather definite conclusions as to the value of this method of corrosion control in sulfide-bearing vapor zones.

In addition to the use by industry of ammonia for pipe line tank vapor space corrosion, this chemical also is being used by some oil producing companies for protection of the annular space of the tubing-casing of wells producing sulfide-bearing oils and gases.[3] Treatment in this latter case is cited as experimental and it is not believed that final conclusions as to its value have been obtained. The method and frequency of treatment centers around the proposition that chemical injection must be infrequent (i.e., one to three times per year) and that sufficient anhydrous ammonia should be added at one time to maintain a condensed water pH of 8 to 12.

Test Data

In evaluating the results of ammonia for corrosion control the data obviously must be compared with the rate of corrosion without ammonia addition. Deck steel for pipe line tanks is usually of $3/16$-inch wall thickness. Corrosion holes develop in 24 to 48 months. The reasons for the fluctuation lie in the variation of hydrogen sulfide in the vapor space, which ranges from 0.10 percent to 7 percent at different stages in the handling of West Texas sour oils, the tank temperature, the frequency of filling, the amount and time of water deposition, the amount of air present, etc. Maximum rates of pitting range from 0.0937 to 0.0469 inch per year.

<small>★ Submitted for publication January 3, 1955.</small>

WALTER F. ROGERS—Chief chemist, Houston Production Division Chemical Laboratory, Gulf Oil Corporation. He received a BS degree in chemical engineering from the University of Pittsburgh in 1926 and the professional degree in chemical engineering eight years later. He began work as a chemical engineer for the Gulf Refining Co., in Port Arthur, Texas, in 1926. In 1927 he transferred to the Gulf Production Co., Houston, to study oil field and pipe line corrosion problems under a fellowship of the Mellon Institute of Industrial Research. In 1948 he became chief chemist of the production division. Mr. Rogers has held a number of high offices in NACE, including the presidency.

Abstract

Four-year tests of the effectiveness of anhydrous ammonia injections into the vapor space of tanks storing sour crude oil indicate that previously unexposed steel is protected for four to eight months. After this time, however, corrosion of the steel exposed to vapors from hydrogen sulfide containing crude proceeds at about the same rate in tanks with ammonia injections as those without it. Ammonia injections appear to have little beneficial effect when injected into tanks in which the steel already has been exposed to sulfide vapors. Analogous results are predicted from injection of ammonia into the casing-tubing annular space of sulfide producing wells.

Ammonia treatment has been conducted at three pipe line stations: Wink, Monahans, and Crane, Texas. The treatment at Wink was instituted in a tank with a newly replaced roof in February, 1950, at the rate of 10 pounds of ammonia per day. The results of coupon testing up to 4.5 months duration are shown in Figure 1 as Tank A and indicate a low corrosion rate over this time interval. This tank roof had been in use for 58 months on December 1, 1954, and as of that time no corrosion holes had appeared in the deck.

Monahans Tanks

The treatment at Monahans was begun on November 6, 1950, on ten tanks utilizing 8 to 12 pounds of ammonia per day. These tanks were used primarily to store West Texas-O'Brien oil which has a low hydrogen sulfide content. As a consequence, tank decks there have a service life of from 7 to 16 years.

At the time ammonia treatment was started two of the tanks had holes in the roofs. In January, 1952, 14 months after ammonia treatment started, holes ap-

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peared in the decks of three additional tanks, indicating continued corrosion attack. Coupon tests were conducted in these tanks for 346 days and never were found to show appreciable corrosion. The evidence from continued roof failures, however, is that the ammonia treatment in these tanks did not materially reduce the corrosion rate.

Tests made in these Monahans tanks definitely showed that the ammonia treatment maintained a deck water pH in the range of 10-11.5 at all times.

Crane Tanks

The treatment at Crane was started on the first tank in July, 1950. Injection of ammonia closely followed extensive repairs to the roof. In making these repairs all of the roof sheets containing holes or appearing seriously corroded were replaced. These sheets consisted almost exclusively of plates in the top portion of the cone roof. Sheets without holes were left in place.

Ammonia was added at the rate of 10 pounds per day. By November 1, 1951, 16 months after treatment started, that portion of the deck section which had not been replaced contained a large number of corrosion holes. Thus, ammonia treatment did not prevent continued corrosion of an already partially corroded deck section.

At the time the ammonia treatment was started, weighed 4-inch x 6-inch steel coupons were hung in the vapor space for test. Coupons were withdrawn at intervals up to 480 days. The results are shown as Tank B in Figure 1. It is of particular interest that these coupons showed negligible weight losses for the first 120 days of test. Coupons removed after 120 days showed weight losses indicative of an accelerated corrosion rate.

Following the failure of ammonia to prevent corrosion of the deck of Tank B the roof of a second tank was completely replaced in June, 1951. In November, 1951, ammonia injection was started in this tank at the rate of 10 pounds per day and increased about May 1, 1952, to 15 pounds per day. At some time during the interval February, 1954, to July, 1954, the roof supports collapsed because of corrosion. In addition, several small corrosion holes had appeared in the top center of the tank deck. Thus, in spite of the injection of 10 to 15 pounds of ammonia per day throughout the period (except for a five-month interval), this roof developed corrosion holes in 36 months.

At the time ammonia treatment was started in this tank in November, 1951, weighed 4-inch x 6-inch steel panels were placed in the vapor space of the tank and withdrawn at intervals up to 480 days. The results of these tests are shown in Figure 1 as Tank C. It will be noted, as for Tank B, that for a considerable interval of time after the tests started (in this case 240 days) the corrosion rate was low enough to be negligible. After this time the corrosion rate proceeded at a greatly accelerated rate.

Causes of Sulfide Corrosion

The results of a study on the causes of sulfide cor-
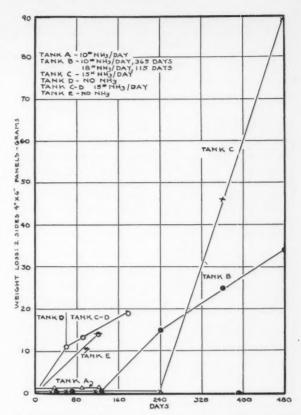
Figure 1—Effect of ammonia on hydrogen sulfide corrosion of steel.

rosion are given in a paper to be published in 1955.[2] This report shows that iron sulfide surfaces are cathodic to steel and once formed are difficult to polarize, resulting in a condition conducive to high corrosion rates.

The data show further that changes in the fluid pH from 4.5 to 9.5, such as result from ammonia treatment, do not greatly change the polarization characteristics of an iron sulfide cathode. These data support the conclusion that treatment with ammonia of a tank having an already developed iron sulfide surface would not reduce appreciably the corrosion rate. This type of result, as mentioned previously, was obtained during the treatment of previously corroded tank decks at Monahans and Crane; it was decided that this phenomena should be studied through the use of coupons.

To carry this out, 4-inch x 6-inch steel panels were placed in the vapor space of a tank handling sour oil at Sand Hills Station and allowed to corrode for 60 days. Several of these panels were then returned to the laboratory for evaluation of the corrosion rate during this time. The remainder were transferred immediately to Tank C at Crane, which was being treated with 15 pounds of ammonia per day.

Coupons were withdrawn at intervals until the roof collapsed in the summer of 1954, terminating the tests even though one coupon was still under test. The results are shown as the Tank D-Tank C curve of Figure 1. It will be noted that the slope of the line

TABLE 1—Time for Penetration of Tanks B and C

TANK	MONTHS TO PENETRATE ³⁄₁₆" STEEL		Pitting Factor for 3 Years Penetration
	Pitting Factor of 2	Pitting Factor of 4	
B	199	99.5	11
C	57	28.5	3.2

TABLE 2—Corrosion Rates of Tanks

TANK	Ammonia Added	Corrosion Rate In Gms/24 Sq. In./Mo./Side
D	No ammonia	2.75
E	No ammonia	1.66
B	10-18 lbs. anhydrous ammonia/day	1.46
C	15 lbs. anhydrous ammonia/day	5.13
D-C	15 lbs. anhydrous ammonia/day	1.06

between 60 and 180 days, a period of 15 pounds of anhydrous ammonia per day treatment, is much greater than the slopes of the curves for Tanks A, B, or C for the first 120 days. It is believed this indicates that the presence of iron sulfide scale on the panels resulted in a much higher rate of corrosion than if the panels had been placed in the vapor space free of sulfide corrosion product.

Pitting Factor for Steel

It is of value to determine whether the high corrosion rates of Tanks B and C are equivalent to the 2 to 4 year corrosion rates for tank steel frequently encountered in the field. Present data[2] show the pitting factor for steel under hydrogen sulfide conditions to lie between 2 and 4. The time for penetration of Tanks B and C is given in Table 1. This is obtained by taking the high weight loss rates of Curves B and C, converting to loss from one side only, and further converting to penetration rate through ³⁄₁₆-inch steel with pitting factors of 2 and 4.

The resulting pitting rates indicate that Tank C even with ammonia corroded at about the normal rate for uninhibited sulfide attack; Tank B corroded at a much slower rate.

In order to furnish an additional means of comparison between the corrosion rates of unprotected and ammonia treated steel coupons, the corrosion losses experienced by 4-inch x 6-inch steel panels tested in a sour oil tank at Sour Lake, Texas, are plotted as Tank E. The corrosion rates of unprotected steel in Tanks E and D can be compared with the corrosion rates of steel in Tanks B and C protected with ammonia. The data are given in Table 2.

These data show that the corrosion losses in ammonia treated Tanks B and C range from approximately the same as found in untreated sour oil tanks to much greater rates than found in non-treated tanks.

Summary and Conclusions

As a result of the field tests made with ammonia in the vapor space of sour oil tanks it is concluded that:

1. The use of sufficient anhydrous ammonia in the vapor space of sour oil tanks to develop pH values in the condensed water of 9.5 to 11.50 will, if the steel tank is initially free of iron sulfide, result in 90 percent or greater protection from four to eight months, during which time a corrosion product of iron sulfide develops.

2. After the development of a coating of iron sulfide of difficultly polarizable characteristics the use of ammonia will not significantly retard the rate of corrosion.

3. If a coating of iron sulfide is present on the steel when ammonia treatment is initiated the treatment will not significantly retard the corrosion rate.

4. The use of ammonia in the casing-tubing annular space of sulfide oil wells will respond, it is believed, in accordance with the above conclusions.

Acknowledgment

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Any discussions of this article not published above will appear in the December, 1955 issue.

that:

Use of Ammonia to Prevent Casing Corrosion*

By H. E. GREENWELL, RADO LONCARIC and HARRY G. BYARS

Introduction

THE PROBLEM of internal casing corrosion above the fluid level needs little introduction. Papers by Battle[1] and Elkins[2] have shown clearly that this probably is one of the greatest corrosion problems yet to face the industry in West Texas and New Mexico.

Typical failure frequency data plotted in Figure 1 were reported by Elkins for the Wasson Field, illustrating that an unprotected casing life of about 12 years could be expected in that field. This was interpreted to indicate a possible expenditure of as much as 90 million dollars if no protective measures were adopted for the remaining life of the field. When one realizes that jeopardy to a major oil reserve is involved when the data are extrapolated to the entire area, it is apparent that the problem is of considerable magnitude.

Corrosion in the vapor space is caused by water which condenses from the gas. The acid gases which always are present dissolve in the condensed water, and each droplet of water becomes a point of corrosion attack. Water first enters the well with the other reservoir fluids and establishes its vapor pressure in the annulus. A temperature gradient exists in the well, and some water condenses on the cooler casing wall near the top. New vapor is replenished from the bottom, and the amount of water condensed depends on the temperature gradient and is independent of the amount of water produced by the well.

Ammonia has been used in small concentration to protect the vapor space of tanks for several years. Although there are significant differences in the two environments, there are enough points of similarity to suggest that ammonia might be effective in wells also. It was probably in this way that the idea of injecting ammonia into wells first occurred. Trial injection of ammonia into wells has been reported and discussed on several occasions as early as three years ago. It was recognized that none of the reported experiments was under sufficient control and that there was no way of evaluating the results.

Theoretical Background

Because of the attractive potential which ammonia offers, it was decided that work should be undertaken to obtain a better idea of the chances of success of the method. It was planned to proceed with sufficient field tests to answer the practical questions of field usage, providing of course that preliminary investigation gave favorable results. The first step in this program was consideration of the theory of the corrosion reactions involved and of the behavior of ammonia under well conditions. Effort was made to

H. E. GREENWELL—Senior chemical engineer in the Production Department of the Atlantic Refining Company, Dallas. He has been with the firm since 1948 specializing in the solution of oil production problems. Mr. Greenwell is chairman of NACE Subcommittee T-1C on Sweet Oil Corrosion and is a registered professional engineer. He is a graduate of the University of Tennessee.

RADO LONCARIC—Chemical engineer with the Atlantic Refining Company, Dallas. He holds a BS in chemical engineering from the University of Ljubljana, Yugoslavia and an MS in chemical engineering from Technishe Hochshule in Graz, Austria. Mr. Loncaric came to this country from Yugoslavia in 1946. He has been with Atlantic for three years in the corrosion group of the Crude Oil Production Department.

HARRY G. BYARS—Corrosion engineer for the Atlantic Refining Company's Dallas-Eastern Region. Mr. Byars received a BS in chemical engineering from the University of Texas in 1953 and joined the corrosion group of Atlantic's Crude Oil Production Division shortly after graduation.

Abstract

The theoretical behavior of ammonia used as an inhibitor in the liquid phase of oil wells is surveyed. Laboratory experiments using a miniature well constructed of transparent plastic showed a special problem would exist if the ammonia were injected too fast, this resulting in formation of solid ammonium bicarbonate and carbonate.

Special injection equipment was constructed and used to inject ammonia into a well without difficulty of any kind. Analysis of produced fluids failed to show ammonia, so gas from treated wells was analyzed to determine distribution of the ammonia. Depths to which the wells were protected was calculated.

Authors say the experiments proved conclusively ammonia will penetrate below the zones of most corrosion; also that the rate of ammonia consumption is low and the reactions occurring should stifle corrosion. Authors' company is establishing a program for ammonia treatment of all unpacked wells susceptible to internal casing corrosion in the vapor space. Cost is estimated at $100 a year.

evaluate leading theoretical questions before attempting any experimental work.

Recognizing that the reactions of corrosion are
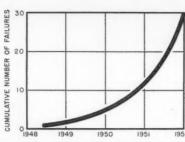
Figure 1—Casing failure frequency in the Wasson Field.

quite complex, it was helpful to simplify the analysis by considering only hydrogen ion behavior. How can a small fraction of the ammonia required to neutralize all the acid gases be expected to prevent corrosion? The answer lies in the following reasoning: Ammonia is much more soluble in water than either hydrogen sulfide or carbon dioxide. The ratio of solubility at typical well conditions is approximately 800 parts of ammonia to three parts of hydrogen sulfide to one part of carbon dioxide. When hydrogen sulfide and carbon dioxide dissolve in the water droplets, the pH drops to a value as low as 4.0, and corrosion occurs. When ammonia is introduced, it goes preferentially into the water and tends to raise the pH value.

Two-Fold Reaction

For purpose of simplicity, this process can be regarded as a two-fold reaction which produces NH_4HS and NH_4HCO_3. Both salts are highly ionized, and both are derived from weak acids. The relatively large concentration of the negative ions (HS^- and HCO_3^-) represses ionization of the acids (H_2CO_3 and H_2S) and increases the pH.

Simplified calculations sufficient to indicate if the process is practical will demonstrate the pH change which can be expected. Because of the high water solubility of ammonia, the amount of ammonia which remains in the gas phase will be neglected. This factor will be considered later in a more detailed analysis. With hydrogen sulfide, a concentration of 0.136 atm. in wells having 1000 pounds per square inch casing pressure has been measured. Using published absorption coefficients for above concentration it is found that 0.351 ml H_2S will dissolve in 1 ml of H_2O. This corresponds to a concentration of 1.46×10^{-2} mols per liter of H_2S in solution. The ionization constant (assuming unit activity) is:

$$\frac{(H^+) (HS^-)}{H_2S} = 9.1 \times 10^{-8}$$

Therefore, $(H^+) (HS^-) = 9.1 \times 1.46 \times 10^{-10}$
$$(H^+) = 3.65 \times 10^{-5}$$
and: $pH \cong 4.4$

It is obvious that, if the term (HS^-) is increased, formation of (H^+) will be repressed by the common ion effect. Introduction of ammonia will serve this purpose. The amount of ammonia required to raise the pH to 8.0, for example, can be determined as follows:

$$(H^+) = 1 \times 10^{-8}$$
$$(HS^-) = \frac{13.3 \times 10^{-10}}{1 \times 10^{-8}}$$
$$= 13.3 \times 10^{-2} \text{ mols/liter}$$

Neglecting the amount of (HS^-) present before ammonia was introduced, ammonia required $= (NH_4^+) = (HS^-) = 0.133$ mol per liter.

Calculations for Carbon Dioxide

Similar calculations can be made for carbon dioxide. The measured average concentration in this case is 4.08 atm. Reduced to concentration in solution, this is equivalent to 14.9×10^{-2} mols per liter. The ionization constant is:

$$\frac{(H^+) (HCO_3^-)}{H_2CO_3} = 3.5 \times 10^{-7}$$

Therefore, $(H^+) (HCO_3^-) = 3.5 \times 14.09 \times 10^{-9}$
$$= 5.21 \times 10^{-8}$$
$$(H^+) = 2.28 \times 10^{-4}$$
$$pH \cong 3.6$$

Again, it is obvious that the (H^+) can be reduced and the pH raised accordingly by increasing the negative ion (HCO_3^-). The amount of ammonia required to raise the pH to 8.0 is:

$$(H^+) = 1 \times 10^{-8}$$
$$(HCO_3^-) = \frac{5.21 \times 10^{-8}}{1 \times 10^{-8}}$$
$$= 5.21 \text{ mols/liter}$$

Neglecting the amount of (HCO_3^-) present before ammonia was introduced:

Ammonia required $= (NH_4^+) = (HCO_3^-) = 5.21$ mols per liter

Adding the ammonia requirements of both carbon dioxide and hydrogen sulfide, 5.343 mols per liter of ammonia in solution is needed. If 15 pounds (400 mols) of ammonia is injected into a well, the pH of $\frac{400}{5.343} = 75$ liters of water will be raised to a value of 8.0. It is reasonable to visualize that 75 liters would represent a maximum amount of condensed water in the casing, and it may be concluded that very nominal amounts of ammonia will give a protective pH.

Protective pH and Corrosion Rates

At this point, it would be in order to consider what constitutes a protective pH. In very general terms, the sensitivity of most corrosion processes to pH has long been recognized. It is axiomatic that increasing the pH of these environments results in a sharply decreased corrosion rate. The well-known use of neutralizers in gas wells attests, as one example, to the effectiveness of pH control. Common use of this principle is made in water systems.

Dr. S. P. Ewing presented data which has a direct bearing on the problem at hand.[3] In studies of the corrosiveness of sulfide solutions, Dr. Ewing found a distinct inflection of the corrosion rate curve at a pH of about 6.0. At more acid values, he obtained

appreciable corrosion rates. At more alkaline values, he found negligible corrosion. In addition, he noted that corroding solutions at pH's below 6.0 became opaque with corrosion products. Above pH 6.0, solutions remained rather clear, although the steel specimens darkened.

Dr. Ewing explained this behavior by considering the dissociation constants of hydrogen sulfide and the solubility product of ferrous sulfide, the presumptive corrosion product. On this basis, he demonstrated that ferrous ions are in excess at low pH values. At high pH values, the sulfide ions are in excess. At low pH's, the excess ferrous ions quickly precipitate sulfide ions, and the zone of precipitation moves out into the solution. This prevents the formation of any protective film on the corroding surfaces.

In the alkaline range, the great excess of sulfide ions precipitates ferrous ions on the corroding surface as they are formed. This quickly stifles further attack. Using the same analysis, he showed that sulfide ion concentration equals ferrous ion concentration at pH 6.72. This "neutral point" agrees very well with the corrosion rates observed in the experiments.

This background was sufficient to convince the authors that pH control had been sufficiently established by acceptable scientific methods to be effective in sour oil wells. The field tests described later in this paper were run without further consideration of this matter. More recently, effectiveness of pH control in this environment has been questioned.[4]

Pre-Corroded Specimens Tested

A simple experiment was designed to obtain additional data on the effect of pH on rate of corrosion in sulfide solutions. Test specimens were pre-corroded in an air-free, saturated solution of hydrogen sulfide. The pH of the corroding solution was in the range of 3.4 to 3.6. The purpose of pre-corroding the specimens was to establish iron-iron sulfide cells, the potential of which was said to control corrosion rate regardless of the pH of the environment.

Pre-corroded specimens then were placed in sulfide solutions having different pH values obtained by adding ammonia to hydrogen sulfide-saturated water. The results are shown in Figure 2. It will be noted that the corrosion rate dropped sharply as the pH was increased. Corrosion rate reached a negligible value at a pH of about 6.0. This result agrees with those reported by Dr. Ewing and by others.[5] Again, it is concluded that raising the pH to values of 8.0 or above may afford control of corrosion in the vapor space of sour oil wells.

This still leaves a number of important questions unanswered. It cannot be said at this point whether or not ammonia will spread downward to protect the corrosion-affected area of the well. Neither is it known what factors will aid and what factors will hinder diffusion. There are also injection problems to face. Finally—and of paramount importance—is the matter of need for procedures of measuring the behavior of ammonia in a well.
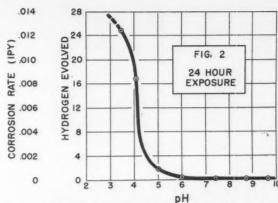
Figure 2—The effect of pH on rate of corrosion in hydrogen sulfide-saturated water.

Laboratory Experiments

Laboratory experiments were set up to examine some of the problems mentioned above before field trials were undertaken. For this purpose, a miniature well was constructed of transparent plastic. The walls were covered with drops of water containing a pH indicator. An atmosphere of carbon dioxide and hydrogen sulfide was introduced, and the indicator assumed the color corresponding to pH 4.0. A series of experiments was run but it will suffice to describe only one here. Ammonia was injected into the top of the "well" equivalent to 0.63 mol percent in the water introduced previously. The water drops at the top immediately changed color, began to collect, and ran slowly downward. At the end of 20 hours, ammonia had penetrated 40 feet to the bottom of the "well."

Other necessary laboratory work included various experiments involving mixing of ammonia and carbon dioxide under different conditions and study and development of suitable analytical techniques. Introduction of ammonia into systems of carbon dioxide, hydrogen sulfide, and indifferent gas at well pressures (up to 1000 pounds per square inch) gave only limited reaction, as predicted.

It was discovered, however, that solid ammonium bicarbonate and carbonate would form in the entrance when ammonia was introduced at a rapid rate. This fact had to be taken into account in designing injection apparatus for field tests. Accepted analytical procedures for determining ammonia and acid gases in the well gases were found satisfactory. However, some special equipment was found necessary, and a number of modifications were made to adapt the analytical methods to the special requirements of this problem.

Field Tests

Laboratory work having disclosed no significant unfavorable factors, the decision was made to employ ammonia injection in a group of test wells in the Wasson Field. Original plans called for testing both flowing and pumping wells under the greatest variety of conditions which could be found in this field. Wells were chosen to represent the various possible combinations of pressure and water production. Sub-

Figure 3—High pressure lubricator used for injecting ammonia.

Figure 4—Closeup of high pressure lubricator in use.
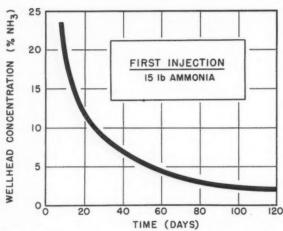
Figure 5—Decline of free casing head ammonia over a period of time.

Figure 6—Decline of free casing head ammonia over a period of time (second injection).

sequently, it was established that ammonia cannot be used generally in pumping wells. Each well reacts differently, and ammonia is lost rapidly from many. Thereafter, only flowing wells were included in the tests.

A high pressure lubricator shown in Figures 3 and 4 was built for injecting the ammonia. The equipment was designed for a working pressure of 1500 pounds per square inch, and all valves were of the full opening type. All equipment, including flexible hoses, was tested to 2250 pounds per square inch prior to use. A detailed procedure was worked out to eliminate the few possible hazards which might exist.

Injection included the following steps: About two quarts of diethylene glycol were poured into the

hose connecting the lubricator with the well. The purpose of the glycol was to sweep all water from the wellhead fittings and prevent the entrance plugging noted in some laboratory experiments. One or two pounds of ammonia then were charged into the lubricator, and this ammonia was bled to the atmosphere. The resulting cooling made full charging by gravity quite rapid.

After charging the ammonia to the lubricator, the ammonia cylinder was disconnected and removed for safety reasons. (Ammonia cylinders will not withstand wellhead pressure.) A cylinder of nitrogen was connected to the lubricator, and a pressure 200 pounds per square inch greater than wellhead pressure was applied. The lubricator was connected to the well, and valves were opened to allow the ammonia to flow into the well.

Analysis of In-Hole Behavior

The actual injection was practically instantaneous in all cases. No plugging occurred and no difficulties of any type were encountered. Some wells were injected with 15 pounds of ammonia, and others with 30. The entire process was, of course, rather time consuming and would not be suitable for injecting large numbers of wells.

The first test of the effectiveness of ammonia injection consisted of periodically determining free ammonia and the acid gases at the casing heads of the wells. In addition, attempts were made to detect ammonia in the produced fluids. Figures 5 and 6 show the decline of free casing head ammonia in several wells over a period of several months. Ammonia was not detected in the produced fluids during the period of test.

It soon became apparent that these data alone would not yield a satisfactory idea of the behavior of ammonia in the wells. The next step consisted of flowing gas from the casing of the wells and performing analyses at intervals during the process. The flow of gas was measured carefully, and the depth from which each sample came was calculated.

Tables 1 and 2 show "blowdown" data from two wells representing the extremes of conditions found. The well shown in Table 1 had the greatest quantity of free ammonia and the well in Table 2 had the least. Original injection was 28 pounds in the former well and 15 pounds in the latter. The "blowdown" data provided the first available basis for actually determining the distribution of ammonia in a well and for establishing practical criteria of protection.

Equilibria Involved

At this stage, one must consider all of the equilibria involved and must enlarge upon an earlier simplified analysis which considered only the formation of NH_4HCO_3 and NH_4HS. Eight components are involved in the process: CO_2, NH_3, H_2S, HCO_3^-, $CO_3^=$, NH_2COO^-, NH_4^+ and HS^-. The equilibria[6] are:

1) $NH_3 + CO_2 + H_2O = NH_4 + HCO_3^-$
2) $NH_3 + HCO_3^- \quad = NH_2COO^- + H_2O$
3) $NH_3 + HCO_3^- \quad = NH_4^+ + CO_3^=$
4) $NH_3 + H_2S \quad = NH_4^+ + HS^-$

Experimental work by Badger and Silver[7] has established that, in effect, the mols of hydrogen sulfide can be subtracted from the mols of ammonia available, and the system treated as if it contained only the one acid gas, CO_2. In this case, only a negligible error is introduced and the analysis is simplified. D. W. Van Krevelen et al[6] developed equilibrium co-efficients for the reactions written above, using a procedure of calculating numerical values for each constituent which can be adapted to our purposes. The prime considerations in this calculation are the material and ionic balance which must be satisfied.

Equations can be written as follows:

5) The ammonia balance
$NH_3 + NH_4^+ + NH_2COO^- = A$ (total ammonia)
6) The carbon dioxide balance
$CO_2 + HCO_3^- + CO_3^= + NH_2COO^- = C$ (total carbon dioxide). CO_2 can usually be neglected in this balance.
7) The carbonate-bicarbonate equilibrium
$K_3(NH_3) (HCO_3^-) = (NH_4^+) (CO_2^=)$
8) The Ionic balance
$(HCO^-) + 2(CO_3^=) + (NH_2COO^-) = NH_4^+$

Using available equilibrium constants, working equations can be derived for calculating numerical values of the constituents.

9) $(HCO_3^-) = 2C - A + NH_3$
10) $CO_2 = \dfrac{K_3 (HCO_3^-) (NH_3)}{C}$
11) $NH_4^+ = C + CO_3^=$
12) $NH_2COO^- = K_2 (NH_3) (HCO_3^-)$

Trial and Error Method

A trial and error method must be used. Knowing the value of NH_3, a value of HCO_3^- is assumed. The other components are calculated, and the correctness of the assumption is checked by the ammonia balance, equation (5). In this way, values of HCO_3^- are assumed until the total ammonia balances. When the correct value is assumed, all of the material and ionic balances will be satisfied. Then, for any depth
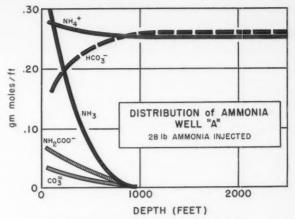
Figure 7—Distribution of ammonia for Well "A."
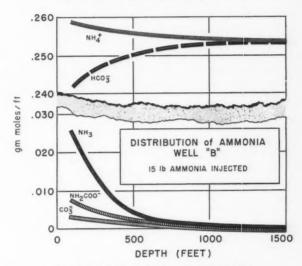
Figure 8—Distribution of ammonia for Well "B."

TABLE 1—Blowdown of Well A

DEPTH	Percent NH₃	Percent Acid Gas
0	7.5	Very slight trace
100	7.1	Very slight trace
250	5.0	Very slight trace
400	2.5	Very slight trace
580	0.8	2.2
800	Trace	4.9
1020	0	5.6
1275	0	5.8
1500	0	5.8

Casing Pressure = 530 pounds per square inch.
Amount of Ammonia Injected = 28 pounds.
Days After Injection = 93.

TABLE 2—Blowdown of Well B

DEPTH	Percent NH₃	Percent Acid Gas
0	0.6	Slight trace
80	0.6	Slight trace
220	0.5	Slight trace
430	<0.1	3.8
550	<0.05	4.8
980	0	5.5
1980	0	5.8

Casing Pressure = 525 pounds per square inch.
Amount of Ammonia Injected = 15 pounds.
Days After Injection = 91.

interval analyzed, the distribution of injected ammonia is known.

The distribution of ammonia was calculated in this manner for two of the test wells. It will be seen (Figures 7 and 8) that at the top of the well NH_4^+, HCO_3^-, $CO_3^=$ and NH_2COO^- ions and NH_3 are present. Free ammonia and $CO_3^=$ and NH_2COO^- ions decline with depth and finally disappear. NH_4^+ and HCO_3^- ions approach the same value, and, at the disappearance of the other ions, become equal. At this point approximately two-thirds of the ammonia originally injected has been accountd for.

By making an overall material balance for the well, it should be possible to estimate the total depth of protection. Referring to Figure 7, it will be seen that NH_3 disappears at a depth of 1020 feet. Therefore, from this point downward in the well, the term NH_3 in equations (5 and (9 equals zero. Then by equations (10 and (12, $CO_3^=$ and NH_2COO^- equal zero, and all of the ammonia must be present as NH_4^+.

Depth of Ammonia Penetration

By making a suitable correction for the small amount of HS^- present and assuming uniform distribution of NH_4^+ at the value indicated when other ions disappear, the depth to which the ammonia penetrated can be estimated. In the well shown in Figure 7, this depth is 2298 feet, which is below the area of most corrosion. The well shown in Figure 8 is protected to 1529 feet, indicating that a somwhat insufficient amount of ammonia was injected. The assumption that ammonia present below the point of disappearance of free ammonia exists as ammonium bicarbonate can be confirmed to a certain extent. The wells blown down to obtain the data cited in this report were blown down again after a few weeks. Small amounts of NH_3 were detected, indicating decomposition of an ammonium compound. There is reference in the literature to the effect that ammonium bicarbonate exerts a negligible vapor pressure of ammonia. Zernike[8] found no ammonia in the gas phase above saturated solutions of ammonium bicarbonate.

Conclusions

It is believed that these results establish conclu-

sively that ammonia will penetrate below the zone of most corrosion. Rate of ammonia consumption is low, and the reactions which occur should stifle corrosion. No significant injection problems exist, and ammonia can be handled rapidly and safely with suitable injection equipment.

Simple criteria of control can be developed from distribution data calculated by the methods discussed in this paper. Additional experience with successive injections should permit determination of the ultimate maximum depth of penetration. It is believed that the well finally will become saturated with ammonium compounds and that it will be necessary to add only enough ammonia to maintain this condition. Surplus ammonia should reach the bottom of the tubing and be produced out. Since the amount of water available for reaction in the gas space is limited, it is considered unlikely that bridges will form in the casing.

Because of the favorable results of this investigation, the authors' company is establishing a program of ammonia injection in all unpacked flowing wells which are susceptible to internal casing corrosion in the vapor space. Injection will be started on the basis of a 25-pound injection at three-month intervals. Economics appear favorable, even if this level of injection has to be maintained. It is estimated that the per well cost will be $100 per year, which compares quite favorably with alternative methods in most cases.

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Any discussions of this article not published above will appear in the December, 1955 issue.

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Electrochemical Studies of the
Hydrogen Sulfide Corrosion Mechanism⋆

By SCOTT P. EWING*

Introduction

ALTHOUGH THE IMPORTANCE of hydrogen sulfide corrosion in the oil industry is well known, a review of the literature has failed to disclose an adequate description of the hydrogen sulfide corrosion process in terms of the electrochemical theory. There are statements to the effect that sulfides in the metal are converted to hydrogen sulfide by acids and that hydrogen sulfide diminishes the anode polarization because it assists the anode process of electric transfer, or in other words, that sulfides are "anodic stimulators."[1] It is the intention here to explain the hydrogen sulfide corrosion process in terms of the well-known physical and chemical properties of the metals and the solution.

While it is economical in some cases to use more resistant and more expensive alloys, the bulk of the sour crudes is now produced, transported and stored in low alloy steel equipment. Much progress has been made to make this possible without excessive corrosion. It also is possible that a thorough understanding of the hydrogen sulfide corrosion mechanism will lead to more effective methods for corrosion prevention.

The usual way to describe the hydrogen sulfide corrosion process in the absence of oxygen is by means of the equation:

$$Fe + H_2S \text{ (aq)} \rightarrow FeS + H_2 \text{ (g)}$$

A similar equation may be written for any other acid, such as carbon dioxide which is very similar chemically to hydrogen sulfide.

It is the intention here to examine the separate anodic and cathodic reactions that occur in hydrogen sulfide corrosion of iron with the hope that if the reasons for the severe attack were fully understood, it might be possible to devise better methods of control. This is the usual procedure for studying many corrosion processes, and it has produced practical solutions in many cases.

Electrochemical Reactions in Hydrogen Sulfide Corrosion

1. *Reactions at Electrodes*

If iron corrodes, the anodic reaction is the solution of iron as ferrous ions. The potential of the iron elec-

Abstract

A statement of the anodic and cathodic reactions in the hydrogen sulfide corrosion process is given along with experimental evidence to indicate that these reactions are the important ones. The corrosion process is explained further in terms of the electrochemical properties of the corroding solution and the corrosion products. Results of laboratory experiments indicate that the description of the mechanism is correct. The possible usefulness of an understanding of the corrosion process is demonstrated by a few practical applications.

trodes (E_A) with respect to the hydrogen electrode, as given in any physical chemistry book[2] is:

$$E_A = -0.440 + \frac{RT}{nF} \log A_{Fe^{++}} \quad (1$$

Where:

R = gas constant = 8.314 joules per degree per mole
T = absolute temperature
F = Faraday constant = 96,489 coulombs per mole
n = valence of ferrous iron = 2
$A_{Fe^{++}}$ = the activity of ferrous ions. Hereafter, activities will be designated as $[Fe^{++}]$

If ordinary logarithms are used and T is 25 C, then $\frac{RT}{F} = 0.05916$.

The writer has made several rough measurements of the volume of hydrogen evolved in the hydrogen sulfide corrosion process; others have made more accurate measurements from carbon dioxide solutions which show that an equivalent amount of hydrogen is evolved in this corrosion process in oxygen-free solutions.[3] It is reasonably certain that when iron corrodes in hydrogen sulfide solutions in the absence of oxygen the cathodic reaction is the deposition of hydrogen. The potential of the hydrogen electrode is:

$$E_c = +0.0592 \log [H^+] - \frac{0.0592}{2} \log P_{H_2} \quad (2$$

The effective voltage or driving force in the corrosion process is then the difference between (1 and (2 which is:

$$E_c - E_A = +0.440 + \frac{0.0592}{2} \log \frac{[H^+]^2}{[Fe^{++}] P_{H_2}} \quad (3$$

2. *Reactions in the Solution*

It is seen that the voltage, $E_c - E_A$, depends on the activity of hydrogen and ferrous ions in the solution
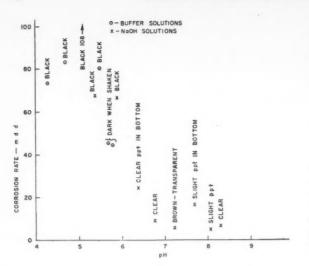
Figure 1—Effect of pH on corrosion rate in solutions of the same hydrogen sulfide activity.

and the pressure of gaseous hydrogen. The ferrous ion content of the solution is controlled by the solubility product of ferrous sulfide as in the equation:

$$[Fe^{++}] \, [S^{--}] = 10^{-19} \tag{4}$$

Ferrous ions will go into solution at anodic areas and will be precipitated as ferrous sulfide when the solubility product is exceeded. This corrosion product, which forms almost instantaneously when a piece of iron is placed in hydrogen sulfide solution, may be considered as always present. Although they do not so state, the experiments of Bond and Marsh indicate rather definitely that in the absence of oxygen the corrosion product is entirely ferrous sulfide.[4] Similarly, the sulfide ion content is controlled by the dissociation constants of hydrogen sulfide:

$$\frac{[H^+] \, [HS^-]}{[H_2S]} = 1.15 \times 10^{-7} \tag{5}$$

$$\frac{[H^+] \, [S^{--}]}{[HS^-]} = 10^{-15} \tag{6}$$

Multiplying (5 and (6:

$$\frac{[H^+]^2 \, [S^{--}]}{[H_2S]} = 1.15 \times 10^{-22} \tag{7}$$

When appropriate substitutions are made in (3, using (4 and (7, the following expression for the driving voltage is obtained:

$$E_C - E_A = + 0.353 + 0.0296 \log \frac{[H_2S]}{P_{H_2}} \tag{8}$$

This equation states that the driving potential depends only on the hydrogen sulfide activity of the solution and the pressure of hydrogen gas or partial pressure of hydrogen. For example, if the corrosion takes place at atmospheric pressure, the hydrogen pressure will have to be atmospheric for hydrogen to be evolved. It may not be obvious why the driving voltage does not depend on pH inasmuch as hydrogen ions are discharged on the cathode at lower potential

in acid solutions. The concentration of ferrous ions in saturated hydrogen sulfide solutions also depends on pH and is greater in acid solutions. The equilibrium relations are such that if the hydrogen sulfide activity does not change, changes in pH will have no effect on the driving voltage.

Experimental Evidence Verifying Reactions

1. *Corrosion Rates and Potentials of Iron in Hydrogen Sulfide Solutions as a Function of pH*

According to equation (8 if the hydrogen sulfide activity and all other factors in the corrosion process are constant and the pH is changed, the corrosion rate should not change. If hydrogen sulfide is bubbled through buffer solutions, the buffer will react with the hydrogen sulfide and its pH will be lowered. If hydrogen sulfide is bubbled through several solutions of different pH until equilibrium is attained, the activity of hydrogen sulfide will be the same in all solutions[5] and the pH will be different. The results of several groups of corrosion measurements in various solutions through which hydrogen sulfide was bubbled are shown in Figure 1. The points designated by open circles represent buffer solutions, prepared by addition of sodium hydroxide to potassium acid phthalate solutions. The pH of these solutions was changed considerably from their original values by reaction with hydrogen sulfide; also the pH of some solutions changed slightly during the corrosion test. The pH values were measured at the completion of the test. The points designated by crosses represent solutions of sodium hydroxide of different concentrations, the most alkaline (pH 8.35) being 10 normal sodium hydroxide. The appearance of each solution at the end of the test is indicated in the figure.

2. *Explanation of Reduced Corrosion Rates in High pH Range*

All of the ions in the solutions referred to above probably had some effect on the corrosion rates but it is clear from Figure 1 that there is a distinct change in the appearance of the solutions and in the corrosion rate at about pH 6. In the lower pH range the solutions soon became opaque due to formation of black ferrous sulfide and the corrosion rates were rather high. Above pH 6 the solutions remained more or less clear although the steel surfaces in all cases were covered with ferrous sulfide and the corrosion rates were much lower.

Since the activity of hydrogen sulfide was the same in all the solutions, equation (8 indicates that the driving potential between anodes and cathodes is the same. Thus, there must be some other explanation for the observed difference in corrosion rates. A possible explanation may be found in the potential measurements shown in Figure 2. The sloping straight lines in the figure are the potentials of the hydrogen and the iron electrodes as calculated from equations (1 and (2. The plotted points in the figure are the observed potentials of steel electrodes which were left in the solutions until their potentials became steady. Obviously the potential of the corroding steel electrode should be somewhere between the potentials of the anodic and cathodic areas on its surface. In the pH range below 6, the slope of the potential-pH

curve approximates the slope of the curves of the unpolarized iron and hydrogen electrodes. Since the current flow or corrosion rate is high over this pH range, the polarization of anodes and cathodes does not change appreciably. In the pH range above approximately 6.5, the corrosion rate is reduced so the current flow is reduced. Since the driving voltage is the same according to equation (8, the circuit resistance must be higher in this pH range. A consideration of the potential measurements in Figure 2 shows that this increase in resistance is on the anodic (iron) areas because the potential of the corroding steel electrode approaches the potential of the cathodic (hydrogen) surfaces as the pH is increased.

A further explanation can be given as to why polarization of anodic areas occurs at higher pH values. From a consideration of the dissociation constants of hydrogen sulfide and the solubility product of ferrous sulfide, in a solution saturated with ferrous sulfide and hydrogen sulfide at atmospheric pressure, the activity of sulfide ions is:

$$[S^-] = \frac{1.17 \times 10^{-23}}{[H^+]^2} \quad (9$$

and the activity of ferrous ions is:

$$[Fe^{++}] = \frac{[H^+]^2}{1.17 \times 10^{4}} \quad (10$$

Hence, in the low pH range the ferrous ions are in great excess while in the high pH range the sulfide ions are in great excess. By setting $[Fe^{++}] = [S^-]$ it can be seen that these two ions have equal activities at pH 6.72. When corrosion occurs ferrous ions are going into solution at anodic areas and are migrating and diffusing away from the anode. At the same time sulfide ions are migrating or diffusing toward the anode.

Precipitation of ferrous sulfide occurs wherever the product $[Fe^{++}] \times [S^-]$ exceeds the solubility product of ferrous sulfide. In the low pH range the ferrous ion concentration greatly exceeds the sulfide ion concentration. The few sulfide ions near the anode therefore are soon precipitated and the zone of precipitation then moves out into the solution where the precipitate does not stifle the anodic reaction.

On the other hand, in an alkaline solution there is a great excess of sulfide over ferrous ions. Hence, any ferrous ions produced at the anode are quickly precipitated as ferrous sulfide on the metal surface. Whether this precipitate is considered as a true resistance, or a barrier to ion movement which produces higher ferrous ion concentration at the iron surface with a resulting change in the potential, is of no great importance. Many of the apparently anomalous observations and data in hydrogen sulfide corrosion may be caused by the removal or adherence of the finely divided ferrous sulfide coating.

The above explanation of the hydrogen sulfide corrosion mechanism accounts for the observations of Figures 1 and 2. The importance of the place of precipitation of corrosion products in controlling the rate of corrosion is widely recognized, but this principle apparently has not been applied to hydrogen sulfide corrosion. This principle further provides a logical explanation as to why high iron content in the pro-
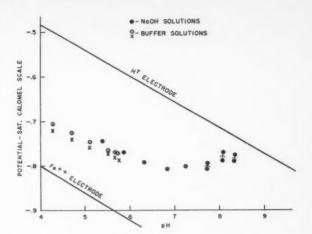
Figure 2—Potential of steel electrodes in saturated hydrogen sulfide solutions as a function of pH.

duced water is an indication of a high corrosion rate in the well and why an alkaline inhibitor might lower the soluble iron content of the produced water and also greatly reduce the corrosion, although it may change the pH only slightly. The expressions for ferrous and sulfide ion content show that if the pH is increased one unit, the hydrogen ion content is reduced ten-fold, the ferrous ion content is reduced one hundred-fold, the sulfide ion content is increased one hundred-fold, and the ratio, $\frac{Fe^{++}}{S^-}$, is reduced ten thousand-fold.

Application of Mechanism to Practical Problems

1. *The Effect of Pressure*

There is considerable evidence of increased corrosion by hydrogen sulfide with increase in pressure. At higher pressures, as in oil wells, the hydrogen sulfide content of the solution will increase, thus lowering the pH. But this is not a satisfactory explanation of the increased corrosion. This statement neglects the fact that if corrosion occurs the partial pressure of hydrogen will also increase, and so, according to equation (8 the driving voltage will not change. Or looking at it in another way, the volume of the consumed hydrogen sulfide is equal to the volume of hydrogen formed so there is no appreciable change in volume when corrosion occurs. Changes in pressure then would have no effect on equilibrium and therefore no effect on the corrosion rate. Some other explanation for the increased corrosion is needed.

When the solution is saturated with hydrogen sulfide at atmospheric pressure, the activity of hydrogen sulfide is about equal to the molality, which is 0.102, so the potential which drives the reaction is:

$$0.353 + 0.0296 \log \frac{0.1}{1} = 0.353 + 0.0296 \, (-1) = 0.324 \text{ volt}$$

The voltage could be reduced by increasing the hydrogen pressure. Calculation of the value of P_{H_2} which will make $E_C - E_A = O$ is found to be 10^{11} atmospheres. It is impractical to achieve this pressure
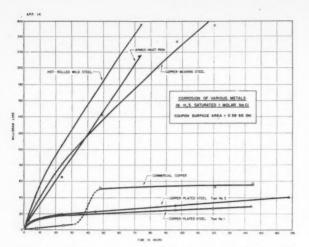
Figure 3—Corrosion measurements of three ferrous metals and copper-plated steel in normal sodium chloride solution saturated with hydrogen sulfide.

but it shows that when hydrogen is evolved in cavities or inclusions in steel, enormous pressures could be produced. Measurements by others have shown that the pressure in these "blisters" is high.

2. Cathodic Protection in Hydrogen Sulfide Brines

It is a generally accepted principle of cathodic protection that corrosion will be stopped if the corroding surface is polarized to the open circuit potential of the anodic areas. This potential is given by equation (1. By substituting the value of Fe^{++} in equation (4:

$$E_A = -0.440 - 0.245 + 0.0296 \log \frac{10^{-19}}{[S^-]} \qquad (11$$

(The value—0.245 is used to change the reference electrode from hydrogen to saturated calomel.) It is seen from (11 that the potential depends only on the sulfide ion activity.

From (7 it is obvious that the sulfide ion activity depends on the hydrogen sulfide activity and the pH. By combining (7 and (11 and assuming that $[H_2S] = \frac{(S)}{34,075}$, the expression for the potential can be placed in the more convenient approximate form:

$$E_A = -0.464 - 0.0592 \,\text{pH} - 0.0296 \log (S)$$

where (S) is the total sulfide content expressed in parts per million of H_2S. The more alkaline the solution and the more sulfide it contains, the more the potential must be lowered to obtain protection. For example, in distilled water saturated with hydrogen sulfide the pH is 3.96, and the sulfide content is 0.204 N or 3480 ppm, so $E_A = -0.804$ volt. In brine from the Trapp pool in Kansas with pH of 6.14 and 290 ppm hydrogen sulfide, the potential is —0.896 with respect to the saturated calomel electrode, or —0.966 volt with respect to the copper-copper sulfate electrode. This potential required for protection has been roughly determined by exposing a group of corrosion specimens with various applied cathodic currents in this brine.[6] It

also appears from potential measurements, which were made in brine vessels protected with magnesium that most of the installations were not protecting the tanks, according to this criterion.

3. The Corrosiveness of Sour Brines

It was shown above that the ratio $\frac{[Fe^+]}{[S^-]}$ indicates whether the ferrous sulfide formed in the corrosion process will be precipitated on anodic areas or out in the solution. Small values of the ratio cause precipitation on anodic areas and a non-corrosive brine. It appears from Figure 1 that a value of the ratio of about one separates the corrosive and relatively non-corrosive hydrogen sulfide brines. This ratio may be expressed in terms of known properties of most brines, that is:

$$\frac{[Fe^{++}]}{[S^-]} = \frac{10^{(25 - 4pH)}}{(1.15)^2 [H_2S]^2} \qquad (13$$

where H_2S is the activity of hydrogen sulfide. The activity is essentially equal to the molality except at high values of pH. For example, at pH 10 the error in the ratio caused by disassociated sulfide ions is only one percent. Obviously the ratio has certain limits of application as, for example, when $[H_2S]$ approaches zero. The driving voltage also must be considered and it approaches $-\infty$ as H_2S approaches zero. Corrosion data on a variety of brines or synthetic brines might provide an empirical way to combine equations (13 and (8 so that the corrosiveness of any brine could be estimated from its composition.

4. The Role of Carbon Dioxide in Corrosion in Brine

Exactly the same type of calculation that was used for hydrogen sulfide may be made for carbon dioxide. Water saturated with carbon dioxide at atmospheric pressure has practically the same pH as water saturated with hydrogen sulfide. The solubility of carbon dioxide is lower but its dissociation constant is greater. The driving voltage for carbon dioxide is about 0.22 volt as compared with 0.32 for hydrogen sulfide. It is believed that experiments similar to those described for hydrogen sulfide would show additional reasons why carbon dioxide is less corrosive than hydrogen sulfide. When both gases are present in a brine, the one which produces the precipitate (ferrous sulfide or ferrous carbonate) will be the one which fixes the protective potential. Unless the hydrogen sulfide content is very low, ferrous sulfide will be precipitated. The presence of any acid or alkali, as carbon dioxide or sodium hydroxide, in a sour brine will not change the driving voltage in equation (8 but it will change the pH and so according to (13 it will affect the corrosiveness.

5. Metallic Sulfides for Reducing Corrosion

The corrosion product in hydrogen sulfide corrosion is usually considered to be non-protective.[7] In these experiments it did not stop the corrosion but it did reduce the corrosion rate in alkaline solutions when it was deposited on anodic areas. It would be desirable to find some means for producing a corrosion product which would be precipitated on anodic areas in acid

as well as alkaline solutions. By the same method that was used for iron, it is found that cuprous sulfide will be deposited on anodic areas at a pH as low as —0.93. This is because of the very low solubility of cuprous sulfide in most acids. This has been given as the reason for the effectiveness of copper content in reducing the atmospheric corrosion rate of steel.[8] Galvanic tests have shown that copper is anodic to steel in hydrogen sulfide solutions. This is also shown from the oxidation-reduction potentials of iron and copper in sulfide solutions. Therefore, if a thin copper coating is plated on steel, the copper will be converted quickly to cuprous sulfide and this material might have some protective properties.

The results of corrosion measurements of three ferrous metals and copper-plated steel in normal sodium chloride solution saturated with hydrogen sulfide are shown in Figure 3. These tests indicate that the thin copper coating has some protective value and there is an indication that a larger copper content of steel might have some value in reducing its corrosion rate in hydrogen sulfide solutions.

Further laboratory and field tests to determine the value of copper as a coating and as an addition to steel are still in progress. Some results indicate that the effectiveness of the copper coating is not impaired when it is applied over a thin layer of ferrous sulfide. The coating might, therefore, be applied to the interior of a pipe line by running a plug of copper sulfate solution behind a pipe cleaning plug. Samples of steels having various copper contents up to one percent are being exposed in a variety of environments containing hydrogen sulfide. At this stage it is certain that copper in the steel has a marked effect in reducing the corrosion rate in some types of exposure. The samples with the higher copper contents also showed much less blistering. There are several other metals whose sulfides are very insoluble and which would be expected to show similar results, but these metals are more expensive than copper.

Discussion

The relations which have been presented have been shown to apply to oxygen-free dilute salt solutions saturated with hydrogen sulfide at atmospheric temperature and pressure. Some corrosion tests have shown that addition of sodium chloride reduces the protective properties of the ferrous sulfide. Some work has been done to determine why oxygen greatly increases the corrosiveness of hydrogen sulfide solutions. It may combine with cathodically formed hydrogen and thus reduce cathodic polarization. It is certain that some sulfates are produced in tanks and in solutions through which hydrogen sulfide and oxygen are bubbled, provided some ferrous sulfide is present. Elemental sulfur is sometimes found in large quantities inside tanks and in laboratory experiments. It is not the intention here to leave the impression

that all the details of hydrogen sulfide corrosion are now understood, but it is believed that methods similar to those described might be useful in helping to explain these processes.

Summary and Conclusions

The electrochemical mechanism of the hydrogen sulfide corrosion process is described in terms of the properties of the iron and hydrogen electrodes, the dissociation constants of hydrogen sulfide and the solubility product of ferrous sulfide. It is found that the driving voltage for the corrosion reaction depends only on the hydrogen sulfide activity of the solution and the partial pressure of molecular hydrogen.

From the electrochemical relations it is possible to calculate the potential required for complete cathodic protection in any sour brine whose pH and hydrogen sulfide content are known. Potential and weight loss measurements on a group of coupons exposed to Trapp brine (Kansas) indicate that the calculated protective potential is approximately correct for this brine.

Corrosion rates of iron in oxygen-free solutions having the same hydrogen sulfide activity but varying pH show that corrosion drops sharply when the pH is above about 7. By calculating the concentrations of ferrous and sulfide ions of the solutions it can be shown that in the high pH range, where the sulfide ion content greatly exceeds the ferrous ion content, ferrous sulfide is precipitated very close to anodic areas. This corrosion product is then effective in reducing the corrosion rate. This is contrary to numerous statements that ferrous sulfide is a nonprotective corrosion product.

A similar study of the solubility product of cuprous sulfide shows that it should have similar protective properties even in weak acids. Laboratory corrosion tests show that a very thin copper coating on steel, which is quickly changed to cuprous sulfide in hydrogen sulfide solution, is effective in reducing corrosion of the steel. The value of the cuprous sulfide coating is being investigated further by means of corrosion coupons exposed in sour crude pipe lines, salt water disposal units and oil wells.

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Reports to Technical Unit Committee T-1J On Oilfield Structural Plastics*

Part 1. Long Term Strengths of Reinforced Plastics Determined by Creep Strengths

By H. D. BOGGS
Fibercast Corporation

Abstract

Creep affects reinforced plastics and is a paramount factor in the determination of long term strength of structural reinforced plastics. It was found that the resins used are the central factor in the long term strength of the product. Creep studies of a given structure using various resins indicate that many resins have the same quick bursting strength but the workable stress loads for long term life vary greatly and in direct relation to comparative values of the resins.

Bond failure, elongation failure and low tensile strength failure are discussed briefly. A method of measuring creep involving the use of an extensometer is given.

ALL MATERIALS are subject to creep under loads. This phenomenon is evident even in metals. Creep in steel when stressed below the yield point and at ambient temperatures is so little that it can be disregarded in most design considerations. But as temperatures are increased it becomes more and more important and at elevated temperatures it is readily measured. Lead on the other hand will show remarkable creep under light loads at room temperatures. Thermoplastics are said to have "cold flow," which is another way of saying that they are subject to creep. Increased temperatures in every case increase the speed of creep.

Creep affects reinforced plastics and once the concept is mastered, it is a paramount factor in determining the long term strength of structural reinforced plastics.

Ultimate tensile strengths, popularly believed to be reliable in gaging reinforced plastics strengths is in fact reliable only when products such as war heads, rocket bodies, etc., which must resist destruction for a *very short* period of time are considered.

As stated, all materials creep under loads—the crux of the problem is to determine what *rate of creep* can be allowed to assure at least a five-year life. Unfortunately with a new material such as reinforced plastics the finding of this data is complex at first. It requires a greater conservatism of thinking because *only time* can finally prove long-term values. Once long term experience has been gained, stress levels will be understood and some up-grading of stress levels will be understood and permissible.

This discussion henceforth concerns reinforced plastics in pipe form. It must be remembered that creep measurement in pipe, which is measurement of the growth of the circumference of the pipe while under water pressure, is just as simple as measuring the growth of a flat plate under tensile load. Stated

percentage growth should apply to many forms and shapes. In fact, the longitudinal growth of the pipe can be measured while a full pipe section is loaded in tension and the results will be found to be as valuable as measurements of the growth of the circumference of the pipe.

Before discussing specific tests and test results, several other things should be understood about reinforced plastics. The fact that reinforced plastics is a composite of thermosetting resins and reinforcing glass fibers makes it necessary to determine which material is the one most subject to creep and therefore, the weakest link of the chain. It is believed that it is the resin.

The glass in a pipe should be thought of as a reinforcing cage. If it is made up of continuous fibers, then it should be supposed further that all fibers are under varying tensions, although the ideal situation is for them all to be under equal tensions. While the fibers themselves have about a 2 percent elongation factor—the cage, because of unequal tension, may require much greater elongation to stress all fibers.

It should be understood also that the resin fills the openings, surrounds the fibers and imbeds them in the resin mass and, it is hoped, bonds them together. If the bond is poor, the pipe weeps, creeps readily and fails under light loads in a short time. This matter is a subject in itself. Many factors which influence it will not be discussed in this paper. It is important, among other things, for the resin to have an elongation factor equal or somewhat greater than that required to put the reinforcing cage entirely under tension. If this is not accomplished then the resin will be stretched and fractured, with early failure

resulting. There are at least 12 such items of importance listed below in the relative order of importance under each heading.

Factors Concerning the Resin:

1. The bond it makes to the glass.
2. The elongation factor.
3. The resin tensile strength.
4. The effect of heat on the resin to glass bond.
5. The effect of heat on the resin tensile strength.
6. The shrink during cure and the percentage of shrink.
7. The resistance to water and chemical attack.

Factors Concerning the Glass:

1. The direction of the reinforcement.
2. The mesh openings, the lay of the fiber and percentage of glass.
3. The finish and absence of foreign matter, including moisture.

Factors Concerning the Process:

1. The cure cycle and system.
2. The explusion of air and gas.

The resin has been found to be the central factor in the long-term strength of the product. Creep studies of a given structure using various resins indicate that many resins have the same quick bursting strength but the workable stress loads for long-term life vary greatly and in direct relation to comparative values of the resins as listed above.

To be sure, changes in the glass affect the workable stress load as well as the quick burst of the pipe; however, if the same glass structure is used in a series of tests with a group of several resins, the resins will rate themselves in a relative order. If the test is repeated, using a different glass structure with the same several resins, the resins again will rate themselves in the same general order. The group results may be up or down compared to the first group due to the change in the glass structure. Creep studies place the proper relative values on all the various factors. Study of ultimate strengths, on the other hand, often leads to erroneous conclusions because it does not bring out the important differences. This is true because ultimate strengths do not bear any relationship to the true long-term strength of the material.

Creep studies at elevated temperatures very pointedly show the weakness of many thermosetting resins. This indicates that certain distortion ratings are a useless value in understanding strengths.

Creep studies indicate the effects of high shrink factors as no other study can. Likewise, the wet strength retention or lack of retention is markedly shown through creep studies and again elevated temperatures are very pointed in revealing weaknesses.

The mechanism of failure, often discussed much

like the fable about the blind men describing the elephant, when viewed from ultimate strength data becomes a clear picture with creep study data. Three types of failure are evident, but it is suspected that there are more. The three types are:

1. Bond Failure—quite evident with many polyesters. Elevated temperatures, far below any so-called heat distortion points, are very damaging to the bond strengths of many resins.
2. Elongation Failure—most evident with brittle and high reactive resins. This shows up in audible cracking and popping in the structure and failure in weeping at low elongation values.
3. Low Tensile Strength Failure—traceable to the resins as one is compared to another in a given glass structure. Many resins lose tensile strength at a rapid rate when a *little* elevated temperature is applied. These again are temperatures far below some heat distortion points.

All the same there is still a need for ways to photograph and observe failures in progress to further understand mechanisms which cause failures. Creep will accurately point out that failures are occuring although the process may take a week or a month or more to finally occur. Such failures cannot be observed as occuring otherwise.

The method of measuring creep is as follows: An extensometer is placed on a pipe, tightened in place and zeroed prior to filling the sample. The extensometer is a band or roller chain placed about the pipe so that as the circumference grows it will extend the band or chain which, in turn, registers the change on a dial micrometer in .001 of an inch. This is a direct reading; therefore it is possible to calculate the growth for any given size pipe equal to a .1 percent, .2 percent growth, etc. through a 1 percent growth.

With better resins tests may be run through a .5 percent growth but the best in the author's experience will withstand 1 percent growth. This failure point will vary by resins and glass structures. The more resin-rich the product, the lower the failure point, etc., so it must be established for each resin and glass make-up.

Present standard procedures are as follows:

1. *Basic Pressure Test—Screening only.*

   Take the readings at one minute intervals at .1 percent through 5 percent growth recording the water pressure necessary to cause the .1 percent, .2 percent, etc. growth. This is done at room temperature and at selected elevated temperatures, say 140 F and 160 F. A new piece of pipe is used for each test and the sample is burst each time after the test and the burst recorded along with the other data.

   If the results compare favorably with other data on file, the next step is to proceed with Test 2.

2. Basic Creep Test—Screening.

A sample is set up, pressurized to a .3 percent growth, readings taken each six minutes for one hour and the growth recorded. Next, the reading is stepped up to .4 percent growth and repeated and so on until at a given percent growth, a growth of .01 percent is recorded from the six minute reading to the 60 minute reading. The next bracket is tested above this point in order to make certain that the absolute maximum point has been reached. Note that the takeup evident the first six minutes is disregarded and likewise if the pipe being tested cannot take .5 percent or more growth, the resin is discarded as not being suitable.

The pressure used at each level remains constant for each level. The pressure at which the .01 percent growth in 54 minutes is observed is rounded out to an even number and this is the test level selected for the 1,000 hour verification level in Test 3. It can be seen by this time that only the best resins have come through to warrant further testing. This test also is run at selected elevated temperatures.

3. Basic Certification Test.

This test is to certify the pipe for more than a 5-year life at the pressure level found in Test 2. If the pipe passes the 1,000 hour test at this level and other tests are satisfactory, it will be rated for service at a maximum operating pressure at one-half this proven pressure level at the given temperature at which the test was run.

Here pressure is maintained on the pipe for 1,000 continuous hours or more and the extensometer readings recorded every 24 hours. These readings are plotted on a log time scale against growth on a straight graph scale. A 5-year slope is plotted from the 120 hour point to the change growth at the 5-year point. The actual readings are plotted on the graph every 120 hours, and the slope of the line from the 480-hour point through the 1,000-hour point projects the slope to extend the experience line through the 5-year point. It is preferable for the intersection of this line not exceed .8 percent growth in 5 years.

Tests that can be made include a creep test for collapse pressure on pipe, a tensile and collapse test to simulate well tubing conditions, and a cycle test which is a violent surge 20 times a minute. Long-term verification racks are used where 20-foot joints are held at the recommended operating pressures for six months to a year with extensometer readings being recorded and plotted for an operating experience line as compared to the verification experience line, etc. Impact tests and other testing means also are used to explain the company's product to the customer and design engineer. This includes chemical resistance testing.

As a final presentation to those who might still believe that ultimate burst data are reliable, data in Table 1 are given. These basic data actually were taken on pipe made by the same process, same reinforcement and wall-thickness but with four different resins.

A study of the data in Table 1 reveals that a safety factor, based on the ultimate burst never could be reliable. There is no doubt in the author's mind that the strength of structural plastics is best explained by systematic creep study; through long-term experience the company hopes to verify that a 500 or 1000 hour test can safely indicate a 5, 10 or 20 year life as the case may be. Among other things, the company develops the proper safety factor to apply to such findings to allow for the unknown factors such as resin and glass degradation.

Part 2. Microscopic Examination as a Test Method for Reinforced Plastic Pipe

By CARL de GANAHL
Spiral-Glas Pipe Co.

Abstract

Microscopic equipment having a magnification power of 20-120 diameters is suitable for distinguishing lack of adhesion in resin to glass from fracturing of resin where adhesion is still satisfactory. Reflected light when shown at 30-40 degrees to the surface of the sample and at right angles to the direction of glass fibers is useful in tests. Photographs are useful to a certain extent but the sample can be examined much better through a microscope with the naked eye.

TWO PARAMOUNT problems generally encountered in producing Fiberglas reinforced plastic pipe are:

1. Adequate permeation and wetting of the glass.
2. Fracturing of the resin on curing the pipe or testing it.

Microscopic examination has proved effective in differentiating between lack of adhesion in the resin to the glass and fracturing of the resin where the adhesion is still satisfactory. Binocular microscopic equipment with magnifications between 20 and 120 diameters is suit-

TABLE 1—Test Data with Four Types of Resins

RESIN USED	Water Pressure at Which Excessive Creep Occurs	Hoop Stress at This Point	Pressure at Which Burst Occurred	Ultimate Hoop Stress	Mechanism of Failure
Resin A......	900 to 1000	5,250	5,600	32,700	Bond
Resin B......	1300 to 1400	7,600	5,600	32,700	Brittle and Bond
Resin C......	1900 to 2000	11,000	5,600	32,700	Brittle
Resin D......	3500 to 3600	20,500	5,600	32,700	Resin Tensile

Figure 1—A section of reinforced plastic pipe. Note the presence of air bubbles.
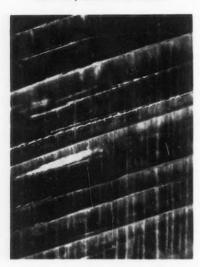
Figure 3—A reinforced pipe section which has been highly fractured circumferentially and lengthwise.

able equipment. It is necessary to have two sources of light available, both of which have rheostat control for intensity, one to be used for transmitted light and the other for light reflected from the specimen.

Transmitted light, while useful on occasion, does not give any identifiable indication of lack of wetting

Figure 2—A section of reinforced plastic pipe. The bare glass appears as thin white streaks.

or lack of permeation. Reflected light, however, when shown at some 30 to 40 degrees to the surface of the sample and at right angles to the direction of the glass fibers will show very clearly whether the resin is adhering to the glass, whether the resin has permeated properly, and whether or not both permeation and wetting are satisfactory. It also will show clearly the fracturing in the resin caused by curing or testing. It is necessary to experiment with the reflected light both as to intensity and angle of application in order to find a clear picture. Also, moving the sample while inspecting it will help.

Photographs are not entirely satisfactory and do not show detail nearly as clearly as can be seen with the naked eye through the microscope; they do, however, give some indication of what to look for. Figure 1, for instances, shows the presence of air bubbles which are quite easily identified. The white streaks, when seen with the naked eye, show very clearly the parting of the resin and the glass.

Figure 2 shows the bare glass quite clearly on the surface as thin white streaks. The white patches indicate poor permeation and also some bare glass. Figure 3 is a picture of a reinforced pipe section which has been highly fractured both circumferentially and lengthwise. The lengthwise fractures show fairly clearly on the photograph. The naked eye can distinguish circumferential fractures from bad wetting more clearly than can be seen from examining the photograph.

A few hours of experience with the naked eye through the microscope is all that is necessary to learn the proper use of the equipment, and it can be extremely useful in determining the source of difficulties.

Some Economic Data on Chemical Treatment Of Gulf Coast Cooling Waters*

A Report of the Recirculating Cooling Water Sub-Committee [1] Of NACE Task Group T-5C-1 on Corrosion by Cooling Waters, South Central Region [2]

1. The Magnitude of the Problem

THIS REPORT is based on information furnished by 16 Gulf Coast refineries and chemical plants. They operate 49 cooling towers with a combined circulation rate of 1,028,400 gpm and dissipate the astronomical figure of 196 billion BTU's per day.

These 16 companies spend $407,000 each year for cooling water treating chemicals. The capacity of the refineries in this group represent 28 percent of the total refining capacity of the Gulf Coast. Assuming that the chemical plants are represented in the same ratio, the total annual chemical cost for the Gulf Coast is $1,500,000. The cost of the chemicals represents only one-third of the cost of treating cooling water (labor, equipment, etc.), thus the total recirculating cooling water treatment costs for the Gulf Coast is $4,500,000. Extrapolating a step further, the Gulf Coast represents about 20 percent of the nation's chemical and refining industry, so the national annual cost for treatment is estimated at $22,500,000.

2. Types of Treatment Used

What is this spent for?

In general, three objectives are accomplished by adding chemicals to cooling water: pH control, scale and corrosion control and algae control. Reports from 25 companies gave the following schedule of chemical use:

2.1 *pH Control*

54 Towers use sulfuric acid
22 towers use caustic
1 tower uses a sulfur burner
1 tower uses waste hydrochloric acid
2 towers use nothing

2.2 *Scale and Corrosion Control*

57 towers use a commercial treatment
24 towers use heavy chemicals

2.3 *Algae Control*

24 towers use continuous chlorination
10 towers use shock chlorination
26 towers use commercial algaecides

Abstract

Based on the reported expenditures for inhibitors used in cooling towers of 16 Gulf Coast refineries and chemical plants, author estimates national cost of inhibitors in the chemical and refining industry to be 22,500,000. Inhibitors are used in cooling water to regulate pH, reduce scale and corrosion and control algae. Materials used include sulfuric acid, caustic, sulfur, glucosates, sodium polyphosphate, sodium dichromate, chlorine and commercial products. Average cost of treating recirculating water on the Gulf Coast is estimated to be $2.21 per billion BTU's. Examples of costs in the three highest and three lowest expenditures reported are given.

The committee will investigate operational and performance factors next.

1 tower uses sodium hypochlorite
1 tower uses no algae control

3. Methods Used in Making Calculations

The daily cost data are based on the following chemical prices:

	$ Per Pound
Sulfuric Acid	0.01
Caustic	0.04
Sulfur	0.025
Glucosates	0.35
Other Commercial Treatments	0.18
Sodium Polyphosphate	0.08
Sodium Dichromate	0.12
Chlorine	0.06

The only useful function performed by a cooling tower is the dissipation of heat, hence all cost and performance data should be tied into the heat dissipating capacity of a tower. As a convenient unit, a billion (10^9) BTU's was selected. The daily value is conveniently calculated by multiplying the gpm evaporation by 0.012.

Figure 1 shows the method used in this study. The tower is from a Gulf Coast gasoline plant, not a member of this group.

4. Average Cost of Treating Recirculating Water on the Gulf Coast

The average cost for pH control is $2.21 per billion BTU's dissipated. Highest cost is $8.13 and lowest $0.11. (See Tables 1 and 2.)

The average cost for scale and corrosion control is $3.97. Highest cost is $9.64 and lowest $0.66.

The average cost for algae control is $1.21. Highest cost is $3.85 and lowest $0.15.

The average total cost for cooling water chemicals is $6.66 per billion BTU's dissipated with a high of $14.06 and a low of $0.66.
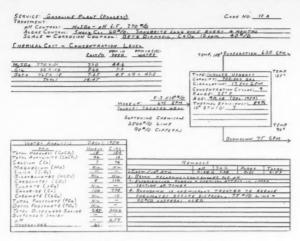
FIGURE 1—Data sheet for gasoline plant tower.

Because of the extremes reported, the cost structure of the three highest and the three lowest cases are analyzed:

Tower No. 2

	10^9 BTU
pH Control (Sulfuric Acid)	$ 2.06
Scale and Corrosion Control (Sodium Dichromate and Sodium Hexametaphosphate)	6.38
Algae Control (Continuous Chlorination)	2.73
Total	$11.16

The pH control cost is slightly below average but the scale and corrosion control cost is quite high. This tower carries the second highest residual (137.4 ppm) of any in the series. The algae control cost is also high because river water which has a high chlorine demand, is used.

Tower No. 4

	10^9 BTU
pH Control (Sulfuric Acid)	$ 8.13
Scale and Corrosion Control (Commercial Polyphosphate-Dichromate)	5.25
Algae Control	None
Total	$11.38

Strictly speaking, this is not a Gulf Coast tower. It is located about 50 miles north of Houston. It uses a very alkaline well water which requires a large amount of sulfuric acid to neutralize. The scale and corrosion cost is higher than average because the blowdown on the tower is higher than average. This is a small tower (4500 gpm circulation rate) and although the cost per billion BTU's is high, the daily cost of treatment is only $3.21. In general, small towers are more expensive to operate (on the basis of heat dissipation) than are large towers.

Tower No. 20

	10^9 BTU
pH Control (Sulfuric Acid)	$ 3.04
Scale and Corrosion Control (Commercial Polyphosphate-Dichromate)	9.64
Algae Control (Shock Chlorination)	1.38
Total	$14.06

This tower carries the lowest pH level in this series, making the acid cost somewhat above average. The scale and corrosion cost is the highest in the

series because it carries the highest treatment residual (138.6 ppm). The cost of algae control is about average.

Tower No. 5B

	10^9 BTU
pH Control (Caustic)	$0.11
Scale and Corrosion Control (Sodium Dichromate and Sodium Hexametaphosphate)	0.55
Algae Control	None
Total	$0.66

Strictly speaking, this tower does not have pH control since it operates at a pH of 7.5-8.0. The scale and corrosion control costs are low because the tower operates at 15 cycles of concentration and loses very little chemicals out the blowdown. The fact that no algae control is used contributes to the low total cost.

Tower No. 23

	10^9 BTU
pH Control (Waste Hydrochloric Acid)	$ 0
Scale and Corrosion Control (Commercial Chromate-Phosphate)	1.13
Algae Control (Own Manufacture)	0
Total	$1.13

This tower is unique in that waste hydrochloric acid is used for pH control and can be given no cost and in that the company manufactures the algaecide used. A very low residual (15.4 ppm) of treatment for scale and corrosion control is carried.

TABLE 1—Cost per 10^9 BTU for Treating Recirculated Cooling Water

Code No.	pH Control	Scale and Corrosion Control	Algae Control	Total
2	2.06	6.38	2.73	11.17
3A	0.22	3.23	1.27	4.72
3B	....	2.16	0.84	3.00
4	8.13	5.25	....	13.38
5A	0.67	2.89	....	3.56
5B	0.11	0.55	....	0.66
5C	....	2.05	....	2.05
6	1.07	5.29	3.53	9.89
8A	0.66	5.96	3.58	10.20
8B	1.50	0.90	3.00	5.40
9	3.57	5.36	1.07	10.00
11 A & B	2.13	2.78	0.89	5.80
11 C & D	0.33	1.88	0.80	3.01
11 E	....	7.96	0.96	8.92
11 G & H	....	3.97	1.65	5.62
12	1.33	3.00	0.15	4.48
14A	2.83	2.97	....	5.80
14B	....	3.22	....	3.22
16A	0.31	1.38	....	1.69
17A	2.36	5.50	0.23	8.09
17B	4.17	4.42	1.09	9.68
18A	0.54	1.04	0.51	2.07
20	3.04	9.64	1.38	14.06
22	1.00	5.85	1.05	7.90
23	....	1.13	....	1.13
24	0.34	1.80	1.38	3.52
Average	2.21	3.97	1.21	6.66

TABLE 2—Towers and Cycles of Concentration

Tower	Cycles of Concentration	Tower	Cycles of Concentration
2	3.55	11E	4.0
3A	7.1	11G	4.0
3B	8.5	11H	4.0
4	3.0	12	3.75
5A	17.6	14A	7.0
5B	15.0	14B	5.0
5C	17.0	16A	2.8
6	3.5	17A	3.5
8A	2.7	17B	4.2
8B	5.5	18A	9.0
9	3.0	20	3.6
11A	4.5	22	3.1
11B	2.5	23	3.5
11C	5.8	24	3.6
11D	5.8		

TABLE 3—Feed Water Analyses in PPM

Tower No.	Total Hardness, CaCO3	Total Alkalinity, CaCO3	Calcium, Ca++	Magnesium, Mg++	Silica, SiO2	Bicarbonates, HCO3-	Carbonates, CO3=	Sulfates, SO4=	Chlorides, Cl-	Total Dissolved Solids	Suspended Solids	pH	Aluminum, Al+++	Hydroxides, OH-	Sodium, Na+	Potassium, K+	Iron, Fe+++
2	127	126	58	6	14	154	0	59	60	292	33	8.1	..	..	..	..	...
3	10	70	4	Nil	9	49	18	Nil	71	...	...	7.0	..	..	..	..	...
6	42	28	24	18	..	....	....	52	35	...	< 5	7.2	0.4	..	..	..	...
9	60	228	44	10	21	278	0	14	40	481	...	7.9	..	..	..	..	...
11	40	12	11	3	14	15	0	75	36	165	10	5.9	2	..	..	..	...
12	120	174	90	30	46	...	...	16	28	...	...	7.3	..	..	..	..	...
14	60	252	14	7	16	...	...	...	204	786	...	7.8	..	..	..	..	...
17A	114	208	78	36	..	...	...	272	474	...	...	7.4	..	..	..	..	...
17B	8	456	4	4	..	...	...	12	282	...	...	9.1	..	..	..	..	...
18	18	46	7	Nil	..	Nil	8	Nil	106	245	...	..	..	..	61	..	...
20	176	180	134	42	12	230	6	22	52	342	Nil	7.2	..	..	42	3	0.3
23	...	...	43	9	5	73	2	43	245	719	3	8.1	..	..	..	..	...
24	120	140	48	14	52	Nil	140	...	64	274	..	7.2	..	..	..	..	1.2*

* Fe_2O_3.

Tower No. 16A

	10⁹ BTU
pH Control (Sulfuric Acid)	$0.31
Scale and Corrosion Control (Commercial Chromate-Phosphate)	$1.38
Algae Control	None
Total	$1.69

This plant is fortunate in having a water of low alkalinity and consequently has a low pH control cost. A rather low residual (14.0 pm) of scale and corrosion control chemicals is carried. And like tower 5B, the fact that no algae control is needed contributes to the reduced cost.

5. Factors Influencing Treating Costs

The first factor influencing the chemical cost of treating recirculating cooling water is the composition of the water used. The more alkaline the water, the higher the cost of pH control. Most of the well water on the Gulf Coast has comparable alkalinities, hence the acid cost is about the same. Feed water analyses can be found in Table 3.

In general, Gulf Coast river water costs less to acidize than Gulf Coast well water, but the increase in chlorination costs is almost exactly equal to the decrease in acid cost.

Naturally, softened water requires less chemicals than does unsoftened water.

The second factor is the type of treatment used. In pH control, the use of sulfuric acid is so nearly universal that it need not be discussed. In the case of algae control, commercial algaecides are somewhat more expensive than chlorination. Continuous chlorination is more expensive than shock chlorination.

In the case of the commercial scale and corrosion treatments, no difference in cost can be found between the phosphate-chromate and the phosphate-ferricyanide treatments. The glucosate type treatment is somewhat more expensive. The cost of heavy chemicals should be somewhat less than commercial treatments but actual operating experience does not bear this out.

The third factor is tower operation. Two general types of operation are used. First, the products to be cooled are pumped to the cooling tower and the cooling sections are in the tower itself. Second, the cool water is pumped to the operating units, through heat exchangers and back to the tower. The first method of operation is the most economical from a chemical requirement standpoint because a lower level of scale and algae protection can be tolerated, hence lower concentrations of treatment are needed.

Most treating chemicals are not used up. They are lost in the blowdown. Thus it goes without saying, that the tower operating with the least blowdown or the highest concentration factor is the most economical from chemical use standpoint.

6. Conclusions

This report has been written strictly from an economic standpoint. It will enable operators to determine whether or not their chemical cost is excessive and point out areas in which the cost can be reduced

The committee will circulate additional questionnaires this year. It is hoped an analysis of the returns from this questionnaire will permit determination of operational and performance factors.

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Four-Year Anode Test Report Is Completed

Performance in Ground Beds Is Covered By Extensive Data

NACE Technical Unit Committee T-2B has completed its final report on a four year project concerning anode performance in ground beds. The title of the report is "Final Report on Four Anode Inspections at Ground Beds Installed by Mississippi Power & Light Company for Committee Test Program." The report covers the findings of the fourth and final annual inspection of the ground anodes taken from four test ground beds installed by the Mississippi Power & Light Company under an anode comparison field test program sponsored by Unit Committee T-2B.

The ground beds, with an original total of 60 anodes were operated with impressed current under close control by engineers of the Mississippi Power & Light Company Gas Department, (now Mississippi Valley Gas Company) with complete operating data taken monthly. The data were furnished to the committee for analysis. In addition, one fourth of the anodes were removed from each bed each year to determine the extent of deterioration. Test results, conclusions and recommendations contained in the report pertain to anode types as tested in soils only and do not cover installations in fresh water, salt water, or other conducting solutions.

The anode beds were so arranged that comparative data could be procured concerning the performance of carbon, graphite and steel anodes in natural soils; carbon, graphite and steel anodes in carbonaceous backfill. Details concerning the ground bed construction were included in the first annual report prepared by the committee which was published and is available as NACE Publication 50-1, First Interim Report on Ground Anode Tests of Technical Practices Committee No. 3, Anodes for Impressed Current.

Accumulated data are contained in the first, second, and third annual reports which contain details of the condition of anodes which had been in operation from one to three years. The second and third reports were not published, but results are reported in the final report.

Results of the four year program give positive indications of relative anode performance. Some types gave excellent service throughout the test period and others showed highly advanced deterioration within the four years. This variation of performance has been great enough to permit reasonable deductions concerning anode performance under installation conditions similar to those encountered in Mississippi.

In addition to relative performance of types of anodes, the report contains a section on installation recommendations. These are based on the findings of the four year test program with additions made by committee members and other interested observers. Installation recommendations cover anode type, ground bed sites, backfill, methods of installation of anodes and backfill.

The report also includes tables showing anode current and net anode resistance for all the anodes over the four

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South Central Region Committee Acitvities Report
More news about activities of NACE technical committees will be found in this issue in the Report on the South Central Regional Meeting. Please turn to this section for information on committees activities at this meeting.

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year period. In addition, charts show average current per anode type in amperes and average resistance per anode type in ohms for each ground bed over the four year period. It is expected this report will be published in full within the next four or five months.
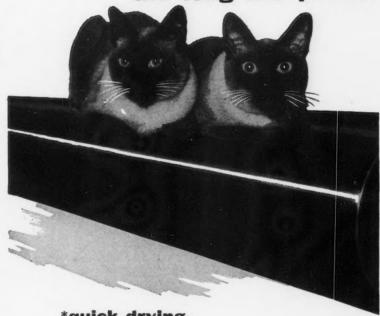
Corrosion Products Bibliographies Readied

Unit Committee T-3B on Corrosion Products, anticipates completion of a first draft of a report on Corrosion Products prior to the 1956 NACE Annual Conference. The report will be a compilation of bibliographies on corrosion products. The success which this committee has achieved in compiling the bibliography is, according to the chairman, A. H. Roebuck, directly at-

Chlorine Bibliography Is Being Reviewed Prior to Approval

NACE Task Group T-5A-4 on Chlorine has completed a bibliography on corrosion by chlorine. Mr. R. I. Zimmerer, chairman of T-5A-4, reported the completed bibliography has been circulated to members of the committee for final corrections or comments. After this final check, the committee will present the bibliography for publication.

The bibliography is composed of 85 abstracts of articles on corrosion by chlorine. It is indexed by materials, and includes abstract numbers applicable. It also is coded according to the NACE abstract filing index.

There are three abstracts on corrosion of aluminum by chlorine, four on carbon graphite, fifteen on ceramics, thirteen on chemical manufacturing chlorine consuming, four on chemical manufacturing chlorine producing, one on chlorine environment with acetic acid, four on chlorine environment with HCL, twenty-seven on chlorine with water, three on inorganic coatings. Also included are four on organic coatings, one on columbium, two on effect of concentration, two on containers, two on copper and copper alloys, four on high ferrous alloys, one on glass lined steel, four on Hastelloy, one on inhibitors, two on lead, three on metals in general, eighteen on general materials of construction, six on nickel and nickel alloys, six on plastics, one on platinum, two on porcelain enamel steel, one on effects of pressure, two on pumps, four on silver, five on silver lined steel, nine on plain carbon steel, three on tantalum, twenty-three on effects of temperature, six on titanium, two on valves and one on zirconium.

The committee has been told additions can be made to the bibliography to cover recent or notable references.

Plastic Jacket Tests Are Now in Fourth Year

NACE Task Group T-4B-5 on Non-Metallic Sheaths and Coatings has reported on committee work and committee tests to date. Committee work includes tests on samples of Neoprene jacket material for lead, iron and aluminum in environments of dilute acids, dilute alkaline and tap water. These samples are in their fourth year of test.

Samples of Neoprene jacket are being tested over lead, iron, and aluminum in acid, alkali and tap water, with one-half volts DC negative on the conductor.

Samples of neoprene and polyvinyl chloride jackets are being tested at room temperatures in synthetic sea water on 90 volts DC negative and positive.

Samples of polyvinyl chloride and polyethylene jackets are being tested in acid, alkali and synthetic sea water at 158 F, 90 volts positive and negative applied to samples in synthetic sea water (3.5 percent NaCl solution).

The task group also has initiated an investigation of the effect of variation in voltage on the rate of failure with

Corrosion Products—

tributable to the activity of its members. Corrosion product bibliographies are being accumulated for the following metals: magnesium, aluminum, titanium, chromium, iron, nickel, copper, zinc, zirconium, silver, tin, lead, molybdenum.

Bibliographies have been completed on the following:

Aluminum: Compiled by H. P. Godard, Aluminium Laboratories, Ltd., Canada.

Titanium: Compiled by R. D. Misch, Argonne National Laboratory.

Iron and Steel: Compiled by M. C. Bloom, Naval Research Laboratory.

Iron: Compiled by N. A. Nielsen and T. Rhodin, E. I. du Pont Company, and E. E. Wicker and G. E. Pellisier, U. S. Steel Corporation.

Copper: Compiled by R. C. Schueller, Phillips Petroleum Company.

Zinc: Compiled by E. A. Anderson, New Jersey Zinc Company.

Zirconium: Compiled by D. A. Vaughan, Battelle Memorial Institute.

Tin: Compiled by the Tin Institute in cooperation with D. A. Vaughan.

Mr. Roebuck has also said that special credit should go to E. L. Simons of General Electric Corporation for his contributions to the committee. The work on the bibliographies will be a continuous effort and committee T-3B will attempt to maintain up-to-date bibliographies on metal systems of interest. Scope of the committee is "to procure, assemble and correlate information on the nature of corrosion products for a better understanding of the mechanisms involved in their formation." Mr. Roebuck invites all NACE members to make contributions to the committee's goal.

In these nickel-clad tanks, phenol synthesized from cumene is kept pure for long periods. Run-down tanks used to check the product against specifications as it comes off stream are also nickel-clad.

Nickel-cladding guards phenol purity in new synthetic plant

With phenol, metallic pick-up alienates customers.

That's why engineers, in designing one of America's newest synthetic phenol plants for Standard Oil Company of California, made these two big storage tanks . . . and three run-down tanks . . . of nickel-clad steel. The synthetic produced is marketed by Standard's subsidiary, Oronite Chemical Company.

Experience over the years has proved that phenol can be stored in nickel or nickel-clad steel for prolonged periods with negligible metal pick-up. Phenol stays premium-market pure, color excellent . . . a big factor in keeping customers for 35,000,000 pounds of product per year happy.
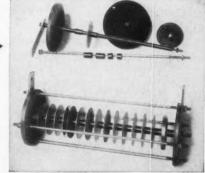
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In many synthetic plants, nickel and high-nickel alloys, such as Monel®, a nickel-copper alloy, are also used in reactors and other items of production equipment. These alloys possess high resistance to corrosion by acids, caustic soda and many other corrosive chemicals.

Do you have a corrosion or purity problem connected with the manufacture or handling of phenol? Write to Inco's Corrosion Engineering Section. They will be glad to give you the benefit of their experience and research without cost or obligation.

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Special Problems Involved in Using Half-Cells In Measuring Lead Sheath Potentials Probed

According to Task Group T-4B-3 on Tests and Surveys, the use of copper-copper sulfate half-cells for pulling through ducts for lead sheathed cables is considered to be a risky undertaking. The committee believes this to be true because the copper sulfate solution which will weep from the half-cell may get on the lead cables through the duct joints and possibly set-up local corrosion on the lead sheath. Should the copper-copper sulfate half-cell be damaged, because of uneven duct joints, and a considerable amount of copper sulfate discharged, possibility of damage probably would be changed to certainty.

This task group has set up a project committee known as Project Group T-4B-3A, whose assignment is to study half-cells. A member of this project group has commented that potential only is not necessarily a safe indicator of a corrosive condition, especially on lead sheathed cables. He says that, for instance, a lead to copper-copper sulfate potential with —0.63 volt and a steel to copper-copper sulfate potential of —0.85 volt might represent satisfactory conditions with no corrosion. The potential of steel to earth can be made more negative than —0.85 volt safely without danger of corrosion.

Environment Is Consideration

The potential of lead to earth cannot be made more negative to earth indiscriminately without taking into consideration the environment surrounding the lead. An increase in negative potential in the presence of chlorides may cause cathodic corrosion due to dissolving of the lead in the caustics that are formed. An increase in negative potential in the presence of chlorides may cause cathodic corrosion due to dissolving of the lead in the caustics that are formed. An increase in negative potential in alkaline environments where the lead is in contact with steel may lead to lead-steel couples in which the lead becomes anodic with respect to steel and will corrode.

Also the potential of lead sheath will be considerably less than —0.63 volt and still be free from corrosion provided the cable sheath surface has become passive. That is, a uniform silicate or oxide film has been formed over the surface of the lead. When this condition prevails, the cable to earth potential will measure less than —0.63 volt to a copper-copper sulfate half-cell. Such a condition may exist in sandy soils. If a new cable is placed along side an old cable, the new cable will be anodic with respect to the old cable and may corrode before a passive film is formed. Corrosion once started is very difficult to mitigate. The passive film will form slower when the cables are under water when corrosion is more likely to start.

Another member of the committee commented that he measures the potential between the cable and a copper-copper sulfate half-cell and also between the cable and a lead electrode. Cable-to-earth potentials to the lead electrode and the copper-copper sulfate half-cell have been found to vary from —0.57 to —0.61 volt. An effort is made to keep the cable at —0.2 volt to a lead electrode. If the lead electrode is moved around in a small orbit, different cable-to-earth potentials can be observed. If a copper-copper sulfate half-cell is used, there is less variation among locations and measurements can be duplicated when repeat measurements are made at various locations in this orbit. It also has been found necessary sometimes to make the contact with earth about 60 feet from the manhole to get outside the local influence of the manhole hardware.

Cleaning Lead Plate Recommended

Another member commented that variations can be obtained by moving the lead electrode from one location to another because of dirt adhering to the lead plate, changes in the film on the lead plate and scratching of the lead plate in handling. This factor can be eliminated by cleaning the electrode or wiping off dirt with a wet rag. Another member of the committee reported that he had observed that polarization potentials develop at the surface of a lead plate. When using the lead chloride half-cell he had found that potentials varying as much as 80 millivolts may be noted between his own measurements and those made by another company. Tests made between a test piece of bright lead sheath 1 x 6-inches and a copper-copper sulfate half-cell

Special Problems—

placed a few inches apart on the earth showed differences of potential of approximately —0.55 and —0.60 volts. When tests are made between the cable sheath and a copper-copper sulfate half-cell in the same location, the potential may be —0.45 volts. One member of the committee said his company is using a lead plate in the manhole and that various negative readings can be obtained by moving the galvanized manhole iron ladder around in the water.

Dirt In Joints Cited

One member commented that the lead chloride half-cell might go bad any time. He had found that there was a constant difference between measurements made with a lead sheath and copper sulfate half-cell and between a lead sheath and a lead chloride half-cell. He discussed duct surveys using a duct slug and commented that the highest cable in a duct slug potential may not be the point of corrosion, namely because of the duct slug to earth resistance. Corrosion can be expected where there are considerable changes in potential or reversal of the cable to slug voltage. Corrosion is usually found in joints in the duct where dirt infiltrates between the joints.

In discussing the need for a design for sheath current measuring equipment, one member commented that he had made many measurements of sheath current by measuring the millivolt drop along a section of sheath then introducing a known current on the sheath in the opposite direction until a millivolt-meter read zero. The known current introduced on the sheath was thus a measure of the current flow on the sheath. A large number of the measurements had been made and the fundamental requirements for the test equipment had been established.

Task Group T-4B-3 has set-up a project group to be known as Project Group T-4B-3B, whose assignment is to study a design for sheath current measuring equipment.

Plastic Jacket Tests—

jacket material. Samples are exposed to 22½, 45, 64½ volts DC negative.

To date it has not been possible to assess the values of jacket materials in preventing corrosion by measuring the change in resistance of wires covered by the jacket material. Within rather narrow limits there is no significant systematic change in the resistance of wires composed of iron, lead, or aluminum protected by jacket material. Apparently the protection afforded by most conventional jacket materials is practically complete until a fault or holiday in the jacket develops. The condition of the protective jacket and its probable service life before developing faults seems to be correlated with its resistance.

Tests now underway and any new tests undertaken subsequently will be followed by means of measurements made on insulations with a general radio megohmmeter. In general the application of voltage has accelerated failures. High voltages accelerate more powerfully and DC negative accelerates greater more than DC positive.

Relatively low voltages are sufficient to cause significant acceleration. Two or three volts per mill accelerates failures very strongly. Dissolved salts in the water in which the samples are soaking under voltage appears to delay failure. This effect has been checked for sodium chloride only.

One member of the committee had discussed results of his laboratory tests on tape coatings to determine the effects of operating conditions on coatings. The tapes are wrapped on a 2½-foot length of 1-inch pipe and submerged in water of 2000 ohm-cm resistivity. A negative potential of 0.85 volt referred to copper sulfate electrode is applied to the pipe for two weeks. This voltage is increased to 1.0 volt, 1.2 volts and so on up to 2.5 volts. Although no detailed results are available, one member has indicated that several polyvinyl chloride tapes appear to be satisfactory when compared to a coal tar enamel coating. Other tapes broke down. A two coat application of liquid Neoprene appears to be performing well.

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Work is now under way on the fifth biennial Bibliographic Survey of Corrosion.

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More than 3500 pages of technical articles were published in Corrosion during its first 10 years.

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An index to the Technical Committee Activities Section in Corrosion is published annually in December.

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Information on the NACE Abstract Card service is cheerfully supplied on request. The cards are sold on a subscription basis. Some back issues are available.

Three Committees Will Meet at San Francisco

Three NACE technical committees will convene during the Western Region Meeting scheduled November 17-18 in San Francisco. T-5A-1 on Sulfuric Acid Corrosion will meet at 8 pm November 16; T-2H on Asphalt Type Pipe Coatings also will meet on November 16 at 8 pm. On November 18, T-4F-1 on Water Meter Corrosion will meet at 9 am. The meetings will be held in the Sir Francis Drake Hotel.

Immediately preceding the Western Region Division Meeting, a three day short course on the "Corrosion Problems in the Process Industries," sponsored jointly by the University of California and NACE, will be held in San Francisco.

Bigos Heads Research Unit

Dr. Joseph Bigos, Director of Research of the Steel Structures Painting Council, Mellon Institute, has accepted the chairmanship of NACE Technical Unit Committee T-6R on Protective Coatings Research. Dr. Bigos accepted the chairmanship on the resignation from the office by Dr. Robert Steiner.

Dr. Steiner had been chairman of the committee since its inception, but with added duties incurred with a change of company affiliation, felt he should resign as chairman of T-6R. Dr. Steiner is now with the Naugatuck Chemical Company.

Dr. Bigos long has been active in NACE activities.

NACE News

Illinois U. Short Course to Be Held Dec. 5-9

CONFERRING HERE about the Southeast Region program at Miami November 10-11 are Joseph Frink, program chairman for the meeting and Joseph B. Prime and Nicholas O. Boutzilo, respectively vice-chairman and chairman of Miami Section.

Southeast Region's Fall Meeting Opens At Miami Nov. 10

Plans have been completed for Southeast Region's November 10-11 fall meeting at Key Biscayne Hotel and Villas, Miami, Fla. Scheduled to be given are 13 papers and a panel discussion.

Motion pictures will be shown, a display of corrosion control instruments will be provided and banquet will be held November 11. Business meetings of Miami and Jacksonville Sections also are scheduled.

Birmingham Section Organized September 30

Seventeen members of NACE met September 30 at the Moulton Hotel, Birmingham, to organize a local section. It was decided by unanimous vote the section be called the Birmingham Section and rules and regulations were adopted.

The following were elected as temporary officers: H. W. Ross, Temporary Chairman; S. A. Gibson, Temporary Vice-Chairman and S. R. Hart, Jr., Temporary Secretary-Treasurer. These temporary officers were also nominated for permanent officers to be voted on after the approval of the section petition by the Southeast Regional Board.

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More than 1400 copies of Corrosion are mailed monthly to addresses outside the United States.

NACE MEETINGS CALENDAR

Nov.

3   Pittsburgh Section. Mellon Institute.

7   North Texas Section, Dallas. Wrought Iron Corrosion.

8   Cleveland Section. Case History of Cathodic Protection Installation, Bernard Husock.

14 Genesee Valley Section. Joint meeting with American Society of Metals.

15 Chicago Section. Engineers' Club. Corrosion and Design, C. G. Munger.

28 Tulsa Section. Corrosion Clinic covering coatings, rectifiers, inhibitors, galvanic anodes.

(Late) Carolinas Section.

Supervisory Personnel Noted at Short Course

A relatively high proportion of the 82 registrants for the September 12-16 Washington University Short Course on Corrosion were supervisory personnel. The course was held at the university in St. Louis, with cooperation of Greater St. Louis Section NACE.

It also was significant that more than 85 per cent had been in corrosion work less than two years and that about 10 per cent had attended other corrosion short courses. The registrants came from 23 states.

Cathodic Protection Is Subject of Second Biennial Sessions

Simultaneous double sections will be scheduled for subjects during the December 5-9 Short Course on Cathodic Protection to be given by the University of Illinois, Department of Electrical Engineering, Urbana. The National Association of Corrosion Engineers is cooperating with the university in giving this second biennial course on the same subject by the university.

Elementary and advanced treatment of basic subjects will be available and laboratory work for beginning and advanced students will be provided. Presentation of the topics will be staggered over the five days to permit maximum personal contact with each instructor. At a final round table discussion registrants will have full opportunity to ask questions of the whole staff. Informal contacts and exchange of ideas is possible at group luncheons also.

Herbert H. Uhlig, president of The Electrochemical Society and director of the Corrosion Laboratory at Massachusetts Institute of Technology will address a banquet Thursday, December 8.

Variety of Subjects
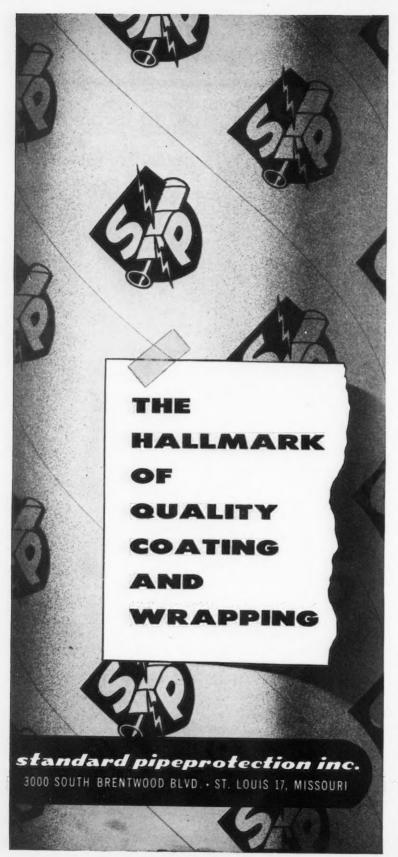
Among the subjects for various lectures and meetings are: Elements of corrosion reduction, elementary corrosion control practices, advanced cathodic protection practices, mathematical methods applied to earth resistance and current attenuation problems, basic electrochemistry.

Coatings — asphalt, coal tar, plastics, paints and varnishes; mathematics of finance, economics of cathodic protection systems, corrosion control organizations, status of research work on cathodic protection, management looks at cathodic protection, elementary instruments laboratory, elementary apparatus laboratory, power conversion laboratory, potentiometric and half-cell laboratory.

In addition to the several guest lecturers, the course will be staffed by the members of and use facilities of the Cathodic Protection Research Laboratory of the University of Illinois. Prof. Ray M. Wainwright is project supervisor and general chairman of the short course. Prof. Walter H. Bruckner is technical director of the Cathodic Protection Laboratory.

Resident university staff members to lecture are: Luther B. Archer, professor of electrical engineering; Harold N. Hayward, professor of electrical engineering; Ray M. Wainwright, associate professor of electrical engineering; Walter H. Bruckner, research associate professor of metallurgical engineering; Herman E. Koenig,

Pittsburgh Learns Value Of Corrosion Committee

Excellent results have been achieved in developing records of bonding and rectifier installations and in cooperative working arrangements among members of the Western Pennsylvania Corrosion Committee. This and other facts about the two year old committee were told to an October 6 meeting of Pittsburgh Section at Mellon Institute by C. J. Erickson, Jr., Peoples Natural Gas Co.

Mr. Erickson explained how the committee was organized to bring together operators of underground plant in Western Pennsylvania to cooperate in the battle against corrosion. There were present 35 members and five guests.

Uses of Ceramic Coatings Told to Boston Section

Nat Cannistraro, general sales manager of The Bettinger Corp., was the scheduled speaker on "Ceramic Coatings at High Temperatures" at a meeting of Greater Boston Section September 28. The dinner meeting was held at Beaconsfield Hotel, Brookline.

The following meetings have been scheduled by the section:

Dec. 7—High Temperature Corrosion, Prof. Grant, Massachusetts Institute of Technology.

Feb. 8—Corrosion of Light Metals, R. R. Cope, Aluminum Company of America.

May 2—Organic Coatings, Kenneth Tator Associates.

Illinois U. Short—

assistant professor of electrical engineering, all of the University of Illinois.

Visiting lecturers will include: Richard Cubbeerly, Flintkote Corp., Whippany, N. J.; Norman Hackerman, professor of chemistry, University of Texas; A. C. Kilberg, Minnesota Mining & Mfg. Co., St. Paul, Minn.; Marshall E. Parker, consulting engineer, Houston; Norman Peifer, Manufacturers' Light and Heat Co., Pittsburgh; Troy Stilley, corrosion and standards engineer, Illinois Power Co., Decatur, Ill.; R. F. Fischer, vice-president, Smith-Alsop Paint Co., Terre Haute, Ind.

Registration Is Limited

Registrations are limited to 50 and will be accepted through November 25. Fee for the short course will be $40, plus $12 for the banquet and five luncheons. Other costs are not included. Reservations for the course and for local housing can be made through R. K. Newton, Supervisor of Engineering Extension, 116D Illini Hall, 725 South Wright St., Champaign, Ill.

ERRATUM

1955 Year Book

Persons who have the 1955 NACE Yearbook may wish to make the following correction: On Page 62, Other Committees—Under Publication Committee the name A. B. McGee should read:

A. B. McKee

Pressurized Water Reactor Described at New York

Design of the atomic plant which Consolidated Edison Company of New York plans to build at Indian Point on the Hudson River was described September 21 by O. G. Hanson, of the company. He spoke to 60 members and 20 guests of Metropolitan New York Section at the Chemists Club, New York City.

Mr. Hanson's talk, illustrated with slides, described the pressurized water reactor, materials of construction and water purification problems.

Other meetings, all but one at the same location have been planned as follows: October 26, December 7, January 25, May 2.

Film on Metallizing Is Set at Schenectady

First fall meeting of the Schenectady-Albany-Troy Section was scheduled to be held Tuesday, October 11, in the Electrical Engineering Building, Union College, Schenectady, New York. The program was to consist of a color and sound film entitled "Metallizing", with comments by a member of the Metallizing Engineering Company, Incorporated.

The section nominating committee also was scheduled to present a report of names of persons to be candidates for officers of the section for the coming year.

Sample Talks on Electrodeposited Metallic Coatings

"Corrosion Behavior and Protective Value of Electrodeposited Metallic Coatings," was the topic of a talk by Clarence H. Sample, The International Nickel Co., Inc., before Kanawha Valley Section September 15. Mr. Sample is chief of the Inco Electroplating Section and chairman of the American Society for Testing Materials Committee B-8 on Electrodeposited Metallic Coatings.

His talk summarized some findings of the ASTM committee on the protective value of zinc, cadmium, copper, nickel, chromium and lead. In most cases base metal was steel.

Scheduled meetings of Kanawha Section are as follows:

November 17—Marietta Country Club, Marietta, Ohio. W. F. Fair, Jr., Tar Products Div., Koppers Co., Verona, Pa., will talk on Protective Coatings for Underground Structures.

January 19—Huntington, W. Va. Wayne W. Binger, Aluminum Company of America Research Laboratories, New Kensington, Pa., will talk on Corrosion Behavior of Aluminum Alloys in Different Chemical Environments.

March 29—Charleston, W. Va. C. H. Gatos, Engineering Research Laboratories, E. I. duPont de Nemours & Co., will discuss Corrosion Inhibitors —Theory and Practice.

May 17—Huntington, W. Va. Raymond B. Hoxeng, Applied Research Laboratories, United States Steel Corp., Monroeville, Pa., will discuss Fundamentals of Corrosion.

The NACE Abstract Card Service is the most extensive collection of general information on corrosion available to its subscribers.

85 Attend Chicago's Ladies' Night Program Opening 1955-56 Season

Annual ladies' night of Chicago Section was attended by 85 members and guests. The meeting was held September 20 at the Engineer's Club and was the first of the 1955-56 season. There were 35 ladies present.

Featured was a motion picture "Flight Into the Future," supplied by Bakelite Div. of Union Carbide and Carbon Corp. Ken Peisker was senior host, assisted by H. G. Prawitz. Protecto Wrap Company was host during the fellowship hour. Chairman H. W. Flournoy introduced distinguished guests and committeemen for the coming year.
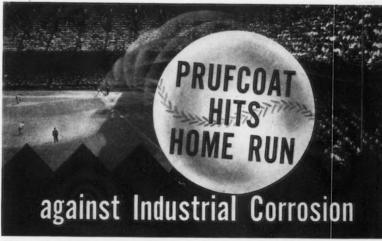
Messrs. Ray Lindberg and William Ewing were elected candidates for regional offices.

Corrosion in Water Flood Is Covered at Dallas

H. L. Bilhartz, president, Production Profits, Inc., Dallas was the scheduled speaker at an October 13 dinner meeting of Shreveport Section. His talk, "Corrosion in Water Flood," told of the part corrosion plays in water flood projects.

Five Technical Committee reports have been published in 1955 by NACE through June.

More than 1600 Corrosion subscribers are not members of NACE.

PERSONS ACTIVE IN THE CANADIAN REGION MEETING at Montreal September 15 are: G. I. Russell, past chairman, Canadian Region; H. G. Burbidge, trustee, Montreal Section and co-chairman Montreal symposium; R. J. Law, director, Canadian Region; Commodore Baker, Constructor-in-chief Royal Canadian Navy, guest speaker; T. R. B. Watson, chairman, Toronto Section; K. N. Barnard, secretary-treasurer, Canadian Region and W. V. Papineau, chairman Montreal Section.

Changes Are Made in Cleveland's Program

The following are changes in the scheduled meetings of Cleveland Section as published in CORROSION, October, Page 78:

November 15—Case History of Cathodic Protection Installation by Bernard Husock.

January 17—Joint meeting with The Electrochemical Society.

February 21—Corrosion in Military Installations, Col. Lindsay M. Applegate.

April 17—Corrosion in Petroleum Industry, L. Mills.

May 22—Stress Corrosion, Julius J. Harwood.

Genesee Valley Features Hot Water Heater Panel

A round table discussion on corrosion of industrial and domestic hot water heaters was featured at the September 20 meeting of Genesee Valley Section. The dinner meeting was held at the Rochester German Club. Twelve members and 6 guests were present.

Participating in the panel discussion were J. Adkin, Rochester Gas & Electric Co.; D. Priest, The Pfaudler Co.; N. Hammond, Aluminum Company of America; W. Fisher, New York Water Service and N. Fuller, Batavia, N. Y., Water Service.

Corrosion in Hydroformer Discussed at Orange

Initial meeting of Sabine-Neches Section for 1955-56 was held September 29 with approximately 40 members and guests attending at Little Mexico Restaurant, Orange, Texas. Glen L. Smith of Cities Service Refining Company spoke on Corrosion Problems in a Hydroformer Unit. His talk covered the general process and physical description of the hydroformer unit and the corrosion and maintenance problems encountered after about a month's operation. The process and problems were illustrated with drawings and slides. Changes, both mechanical and operational that were made to remedy these problems were discussed.

Next meeting of the section was scheduled for October 27, with the technical subject to be discussed "External and Internal Coatings of Storage Tanks."

Two Topics Are Discussed At San Diego September 11

Eighteen members and 23 guests heard Arthur E. Burns, chief chemist for Hart & Burns Co., and James Kittredge and Eugene Corcoran of Scripps Oceanic Institute, LaJolla speak at the September 14 meeting of San Diego Section. Mr. Burns spoke on A Paint Chemist's Approach to Corrosion and Messrs. Corcoran and Kittredge on Corrosion of the Reserve Fleet.

Mr. Burns, who also is vice-president and technical director of his company, a subsidiary of Devoe and Raynolds, discussed manufactured paints and their use in corrosion prevention.

Messrs. Kittredge and Corcoran talked about the Third Fleet in San Diego Bay and the effect of bay sewage pollution on the ships. Serious corrosion of ships is taking place at the water line, they maintained, and it has been estimated the Navy is spending $1 million annually in efforts to combat it. Cathodic protection has materially reduced or stopped the corrosion in some cases.

Diversified Program Scheduled at Western Region Fall Meeting

The November 17-18 fall meeting of Western Region will feature a technical program devoted to pipe lines, ocean going vessels, oil field structures and special materials of construction. The meeting will be held at the Sir Francis Drake Hotel, San Francisco.

Meetings of NACE technical committees interested in sulfuric acid, water meters and asphalt type underground coatings are planned.

The meeting follows immediately a three-day course on Corrosion Problems in the Process Industries to be held at Berkeley by University of California, November 14-16 inclusive.

San Francisco Section Hears Talk on Ceramics

San Francisco Bay Area Section held a joint meeting with the American Ceramics Society September 26 at Spenger's Fish Grotto in Berkeley. There were 25 members and 55 guests present to hear S. W. Bradstreet, Armour Research Foundation talk on "Solution and Flame Ceramics."

Mr. Bradstreet discussed ceramics developed primarily for high temperature applications. Possible use of the ceramics as corrosion-resistant materials is being investigated. While they have a natural porosity, this can be overcome by mixtures and by applying unlike coatings over bases, he said.

ASTE Meets in March

The March 19-23, 1956 annual meeting and exposition of the American Society of Tool Engineers will include a program of about 60 papers in 30 sessions at Chicago.

Oklahoma Corrosion Short Course Set Apr. 3-5

Central Oklahoma Section will sponsor in cooperation with the University of Oklahoma an Annual Corrosion Control Short Course at the University Extension Study Center, Norman, Oklahoma, April 3-5, 1956.

Plans are being made to have demonstrations, pictures and talks that will be of particular interest and help to field men, foremen and corrosion control supervisors, as well as technical papers for the benefit of corrosion engineers.

Lehigh Valley Section Elects New Officers

At a recent meeting of Lehigh Valley Section the following officers were elected for 1955-56: J. B. Godshall, Ingersoll-Rand Company, chairman; J. P. Beiswanger, Easton, Pennsylvania, vice-chairman; S. C. Frye, Bethlehem Steel Co., secretary-treasurer.

Also named were the chairmen of the following committees: Program—J. P. Beiswanger; Arrangements and Publicity —J. C. Bovan; Membership—R. Graver.

Alamo Section Elects New Officers for 1956

At a recent meeting of Alamo Section the following officers were elected for 1956: C. M. Thorn, Southwestern Bell Telephone Co., chairman; C. R. Goodrich, Consultant Engineer, vice-chairman; W. W. Elley, Southwestern Bell Telephone Company, secretary-treasurer.

Mitchell Talks on "Hot Applied Coal Tar Enamels"

"Hot Applied Coal Tar Enamels" was the subject of a talk by Malcolm Mitchell of Reilly Tar and Chemical Corporation before 19 members and five guests of North Texas Section October 3. Mr. Mitchell showed a short motion picture on the application of coal tar enamels.

81 Plan to Exhibit at New York Conference

Eighty-one exhibitors already have indicated they plan to participate in the 1956 Corrosion Show at Hotel Statler, New York. The show will be held March 12-15 in conjunction with the Twelfth Annual Conference of the National Association of Corrosion Engineers.

Contracts and specifications will be mailed to prospective exhibitors before October 14. The 123 booths will be located in the Main ballroom, East Room, West Room, Rotunda, Georgian Room and Georgian Room foyer. Copies of the contract can be obtained from A. B. Campbell, National Association of Corrosion Engineers, 1061 M & M Bldg., Houston 2, Texas.

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Registrants From 10 States Attend Permian Tour

About 1000 Miles Covered by 137 In 3-Day Event

The opportunity to see corrosion problems under actual operating conditions brought 137 corrosion specialists from 10 states and Canada to the Sixth Biennial Permian Basin Corrosion Tour, held Oct. 12, 13 and 14. In all seven field trips were held, covering approximately 1000 miles.

Registrants came from Texas, Illinois, Oklahoma, Louisiana, Arkansas, Pennsylvania, Ohio, Missouri, New Mexico and Minnesota and from Alberta, Canada. Effectiveness of various corrosion preventive methods such as use of inhibitors, internal coating of pipe in place using plastics, use of anodes, plastic pipe, various metals and other preventive means were shown on location. Types of equipment included tanks, piping, heaters, tubing and pumps.

John Watts, Internal Pipe Line Maintenance Co., chairman of the Permian Basin Section, NACE, made the welcoming address. Wednesday and Thursday evenings, a discussion was held on the various things seen during the day's tour.

Joseph Rench, Napko Paint and Varnish Co., Houston, spoke Wednesday evening and Charles W. Elwell, the Western Co., Midland, addressed the Thursday evening meeting. Chairman for both meetings was Tom Modgling, Aquaness Corp. and the moderator was Harold Winston, Gulf Oil Corp.

All meetings were held in the Lincoln Hotel.

C. C. Michel, Cardinal Chemical Co. was master of ceremonies at the Friday noon barbecue in the Ector County

Canadian Corrosion Symposium Attracts Over 165 Registrants

A corrosion symposium was held in Montreal September 15-16 under joint sponsorship of Montreal Section, National Association of Corrosion Engineers, Protective Coatings Division of Chemical Institute of Canada and the Associate Committee on Corrosion Research and Prevention of the National Research Council. Eleven speakers presented papers and round table discussions were held on metallurgical problems, cathodic protection, and protective coatings.

Over 165 registered for the symposium. High interest was indicated in the number of questions asked at the conclusion of each paper.

Following luncheon September 16 a film "The Kitimat Story" was presented by Aluminum Company of Canada.

The 1955 Canadian Regional Meeting of NACE was held on the evening of September 15. At this dinner meeting, Commodore R. Baker OBE Constructor-in-chief of the Royal Canadian Navy spoke on "Corrosion Prevention

SCENES AT PERMIAN TOUR—(Top) L. E. Huffman, L. G. Sharpe nad Lonnie Hinds are shown inspecting a coated strainer basket in service since April 1951. Uncoated strainers last only 8 to 10 months. (Middle) Don Bunnell paints to a leak in a plastic tank erected in August 1954. Leak apparently is due to faulty construction. (Bottom) Four-inch plastic gravity pipe line installed November 1951 was moved to another location. During moving solvent spilled on the pipe and caused hardening of plastic and eventually leaks. Stripe seen was applied to pipe during original installation and is virtually intact. (Left) Tubing from a well treated with inhibitor of internal casing corrosion is examined.

Copper Alloys Corrosion Is Ohio Valley Topic

Corrosion and Prevention of Corrosion of Copper Alloys was the October 6 subject of Wilson Lynes, Revere Copper and Brass Co., Rome, N. Y., at a meeting of Ohio Valley Section. Basic Types and causes were discussed and illustrated with colored slides. Methods of prevention were shown.

At a November 8 meeting John Thomas, Jones-Dabney Co., Louisville, Ky., is scheduled to talk on Protective Coatings—Use of Epons as Protective and Maintenance Coatings. The election of officers will be held also.

Canadian Corrosion—

in the Royal Canadian Navy." Commodore Baker has been responsible largely for the development of Canada's up-to-date destroyer escorts of the St. Laurent class and of other new ships. Since July 1948 he also has been chairman of the navy's Committee on Corrosion and Fouling, which reviews the navy's corrosion problems and suggests remedial actions.

T. R. B. Watson was acting chairman of the meeting on the absence of L. W. Shemilt.

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Corrosion is indexed annually in December.

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Over 1000 Register for South Central Meeting

Houston Gathering Far Exceeds Advance Attendance Estimates

Registration exceeded 1000 at the October 18-21 meeting of South Central Region at the Shamrock-Hilton Hotel, Houston. This was some 300 more than had been expected and resulted in a shortage of badges and programs. Meeting rooms, especially committee rooms were filled to overflowing.

Twenty-five technical committees convened.

At the Fellowship Hour Wednesday evening approximately 700 were present. There was excellent attendance at the South Central Region anniversary luncheon and at the Tenth Anniversary Celebration dinner Thursday night.

Attendance at presentation of technical papers was excellent, paralleling the registration.

Among the events of importance was presentation of certificates to past chairmen of South Central Region and an address by the NACE President Frank L. Whitney, Jr., of Monsanto Chemical Company.

Technical committees reported the following:

A task group of Unit T-1C under chairmanship of Joy T. Payton, presented a report on sour oil well corrosion at the meeting of T-1. It is planned to submit the report for publication.

Unit Committee T-5E on Stress Corrosion Cracking of Austenitic Stainless Steel was organized under leadership of L. M. Rogers, Carbide and Carbon Chemical Company, who will act as chairman pending an election.

About 75 attended a meeting of Unit T-2B on Anodes for Impressed Current. A report of a task group organized to work with a National Electrical Manufacturers Association committee will be submitted for publication.

Unit Committee T-2C heard a report on the cathodic protection of cast iron. Several members of the committee are participating in a program designed to provide suggestions of minimum requirements for cathodic protection.

Unit Committee T-2E made final plans for its coupon test program. Coupons have been ordered and will be distributed soon.

Unit Committee T-2D has completed a revision of the standard for measuring electrical conductance of coating on a buried pipe line.

(EDITOR'S NOTE: More reports on committee and other activities at the South Central Region meeting will be published in December.)

Persons requiring back issues of Corrosion are urged to inquire in advance about their availability because many issues are exhausted.

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The NACE Abstract Card Service is the most extensive collection of general information on corrosion available to its subscribers.

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Up to five cross-indexes per card are possible with the random number system used on NACE Abstract Cards. More can be used on duplicate cards.

COMMITTEES MEET AT HOUSTON—(top) R. McFarland and C. G. Munger preside at T-6A session; (second) L. P. Sudrabin discusses work of T-2C; (third) Ivy M. Parker, seated, right, tells T-2E of progress on coupons; (fourth) L. M. Rogers, at table, right; considers report on T-5E work; (bottom) T. J. Maitland, chairman, seated left and T. J. Hull, standing, discuss work of T-2B.

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General News

British Corrosion Group Has Over 400 Members

The British Society of Chemical Industry's Corrosion Group now has more than 400 members. At a general meeting of the group April 27, it was reported that several successful technical events were held during the 1954-55 season, including a lecture by F. L. LaQue of The International Nickel Co., Inc., on "Attention to Corrosion in USA." Other activities included discussions of microbiological activity, prevention of corrosion in the home, the telecommunication industry, boiler plant and recent research on inhibitors of corrosion by acids.

The January exhibition on "Corrosion Prevention in the Home," was attended by 220 members and their friends; a symposium March 31-April 1 on protection of structural steel attracted 320, including 150 non-members.

The educational panel has been expanded and has been successful in promotion of a number of lecture courses at technical colleges and of the first British residential summer school on corrosion at Battersea Polytechnic in July 1954.

The publication committee expects to announce soon a statement concerning conventions on the use of electrochemical terms. A European Corrosion Union still is under consideration.

Planned to be held are a Symposium on Corrosion Prevention in Packaging and Storage at Birmingham, probably during April and a discussion on the Protection of Cable-Sheathing in London during November. A joint meeting with the Sterlingshire Section in March will be devoted to water treatment. Other subjects will be discussed at other sessions.

Titanium Sheet Forecast By U. S. Navy Researcher

An extensive program of titanium sheet rolling will be initiated in the next few months, according to N. E. Promisel, chief metallurgist of the Navy Bureau of Aeronautics. He spoke September 12 at New York University's College of Engineering on the first day of a week's program on titanium.

Mr. Promisel indicated that recent improvements in techniques may lift the manufacture of titanium to the position of a big metal industry with an anticipated price of $1 to $1.50 a pound. Commercial uses of titanium in the chemical industry to meet corrosive conditions is growing as it is in the food handling industry. North America is estimated to have reserves of 100 million tons of the metal with largest quantities in Quebec.

Automation Show Set

The Second International Automation Exposition will be held November 14-17 at the Navy Pier, Chicago.

Atomic By-products Use For Food Preserving Seen

Use of atomic waste by-products to irradiate food and reduce the $300 million annual loss by insect damage was predicted by L. E. Brownell, supervisor of Fission Products Laboratory, University of Michigan. It costs $6 a ton to treat flour, he said.

A challenge to engineers is presented in the field of reactor design, according to B. V. Coplan and J. K. Davidson, of General Electric's Knolls Atomic Power Laboratory.

Turbo-superchargers being used on natural gas lines have made it possible to deliver the gas to consumers cheaper, believes E. G. Beardsley, vice-president of Clark Brothers Co.

Small gas turbines have a promising future because of their simplicity and low maintenance cost despite their high fuel consumption says P. L. Ward, Solar Aircraft Co.

All statements were made during presentation of papers at the Lake Placid, N. Y. national meeting of the American Institute of Chemical Engineers.

Plastic Modified Papers Discussed at Tappi Meet

"Plastic Modified Functional Papers" will be the theme of a November 14-15 meeting at Brooklyn Law School, 375 Pearl St., Brooklyn, N. Y. The meeting, sponsored by the Plastics Committee of the Technical Association of the Pulp and Paper Industry, is open to all interested persons without fee.

Included in the program are the following papers:

Kraft and Synthetic Fiber Pulp Mats for Laminates, L. P. Wenzell, Celanese Corp.

A Preliminary Investigation of the Paper-Laminate Property Relationship, George Shaw, Taylor Fiber Co.

Titanium Organic Polymers and Their Use with Fibers, H. C. Brill, E. I. duPont de Nemours & Co.

Polyesters, H. L. Gerhart, Pittsburgh Plate Glass Co.

Epoxy Resins and Their Use with Fibers, P. A. Thomas, J. L. Welch, Jr., and B. E. Godard, Bakelite Div., Union Carbide and Carbon Corp.

Physical Properties of Papers Coated with Polyethylene by Extrusion, Kenneth A. Arnold, St. Regis Paper Co.

A Comparison of Polyethylene and Polyethylene-Wax Paper Coatings, John C. Rice, Lowe Paper Co.

Instrument Society Meeting

Instrument Society of America will hold its 11th Annual Instrument-Automation Conference and Exhibit at the new coliseum building, New York City September 17-21, 1956.

Citric Acid Removes Scale from Condensers

Frequent descaling of seawater evaporators with citric acid will permit control of scale in seawater condensers, Army Engineers report. Research conducted by the Corps of Engineers, in cooperation with government and private agencies shows that immediate descaling with citric acid in hot brine will return an evaporator to service within an hour. Production has been increased 20-fold by this method with up to 10,000 hours operation without other descaling.

Details of the process are given in PB 111569. "Water Treatment. Prevention of Scale in Sea Water Distillation," 1953, available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. The 130-page report is priced at $3.25.

Magnesium Anode Puzzles Army Demolition Team

An Army demolition team was unable to identify a magnesium anode which fell from a Manufacturer's Light and Heat Company truck in East Liverpool, Ohio. The anode, packed in a bag of backfill, was an object of considerable alarm when discovered near the entrance to Riverview Cemetery in East Liverpool.

The chief of police called Ft. Hayes, an army post near Columbus, Ohio, and a demolition team was sent. Apparently the team was not satisfied with identification of the anode by officials of the light company, because they sent the anode to Pittsburgh for further study.

LPG Impractical As Solution of Smog Hazard

The use of liquefied petroleum gas as an alternae fuel to power motor vehicles in order to reduce smog is impractical, the Air Pollution Foundation, Los Angeles, reports. Tests conducted by the foundation and reported in a publication titled "Feasibility of Control Methods for Automobile Exhaust" indicate that requiring vehicles to use LPG would not reduce smog and would be prohibitive as to cost.

Alcohol-gasoline mixtures do not markedly reduce hydrocarbon emissions, the report indicates.

The foundation believes the greatest promise in lessening auto fumes lies in the use of catalytic converters or afterburners or a combination of a fuel shutoff device and improved car maintenance.

●

Persons requiring back issues of Corrosion are urged to inquire in advance about their availability because many issues are exhausted.

TEST

Building Industry Lists Weather Data Needed

The kind of weather data needed by the building industry to supplement existing information is outlined in a report issued by the Climatic Research Committee of the Building Research Advisory Board. The report has been transmitted to the U. S. Weather Bureau.

Supplementary data needed includes: Monthly reporting of hourly wet-bulb temperatures, cumulative summaries of summer and winter dry-bulb and wet-bulb temperatures, cumulative summaries of rainfall and snowfall and 30-day forecasts. Data are sought on soil temperatures and freezing temperatures.

Battelle Completes Building

A new $1.4 million chemical building has been completed at Battelle Memorial Institute, Columbus which provides 50 percent more space for chemical research.

The institute has completed also the first of three major units in its new atomic energy research center known as the "hot cell" laboratory. It is the first of its capacity to be constructed without federal funds. Ultimate investment of $3.5 millions in atomic energy research facilities is contemplated.

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BAKE

BOOK REVIEWS

A Note on the Efficacy of an Apparatus for the Magnetic Treatment of Water. (In French) 15 pages mimeographed, 8¼ x 11¾, paper. May 30, 1955. By J. Laureys, J. Van Muylder and N. Pourbaix. Centre Belge d'Etude de La Corrosion, 21 Rue des Drapiers, Brussels, Belgium. Price not indicated.

The report covers reproducibility of results, and influence of magnetic treatment on Brussels water, including pH, iron content, and morphology of carbonate and calcium chrystals. Also included are notes on the effect of magnetic treatment on the functioning of a still.

Major Activities in the Atomic Energy Programs, January-June, 1955. 160 pages, 6 x 9 inches, paper. July, 1955. Superintendent of Documents, United States Government Printing Office, Washington 25, D.C. Per copy, 50c.

A semi-annual report of the United States Atomic Energy Commission. Usual information is included on raw materials, production, construction and supply, community operations, reactor development, physical research, biology and medicine, organization and personnel, inspection, patents, civilian application and industrial information. Eight appendices give information on organization, staff, research projects, a report on high-yield nuclear explosions, etc.

Investment Casting Institute Committeemen Are Named

Appointments by Ted Operhall, Misco Precision Casting Company, president of the Investment Casting Institute have been made as follows:

Roger Waindle, Wai-Met Engineering Co., has been named chairman of the institute's Metal Specifications Committee.

V. S. Lazzara, Casting Engineers, Inc., has been named chairman of the Program Planning Committee for the ICI annual meeting this fall.

Standards For Hot Water Heaters Will Be Studied

Reasonable service life for hot water heating equipment is the first objective of a group named to study criteria for performance standards for domestic hot water heating equipment. The Building Research Advisory Board said Dean F. M. Dawson, College of Engineering, State University of Iowa, Iowa City will head the group.

ASTE Program Chairman

Col. Leslie S. Fletcher, Director of the American Society of Tool Engineers' research fund has been named program director for the society's 1956 annual meeting technical sessions. The meeting will be held March 19-23 in the Chicago International Ampitheatre.

NEW PRODUCTS — Materials — Service — Literature

Johns-Manville will divide its present Industrial Products Division into three new operating divisions: The Pipe Division, Packings and Friction Division and Industrial Insulations Division. Robert F. Orth will be general manager of the pipe division; Francis J. Wakem, industrial packings division and Don L. Hinmon, industrial insulations division. The change is effective January 1.

•

Texsteam Hydrogen Probe, a device intended to give warning of dangerous formations of molecular hydrogen within steel structures, has been developed by Texsteam Corp., 320 Hughes St., Houston 11, Texas. The device consists of a steel tube which can be inserted into the vessel through a fixture which includes a valve. The device may be inserted and removed without interrupting the service of the vessel. Atomic hydrogen can migrate readily through a specially designed thin section of the probe and cause formation of blisters in this section. When these blisters break the hydrogen imprisoned in them is released into the interior of the tube and the resulting pressure is recorded on a gauge set into the end of the tube. The theory of operation is that blisters will form much more quickly in the probe than in the thicker walls of the vessel and that the warning given will be adequate to permit operators to adjust the contents of the vessel or take other precautionary or remedial measures.

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All-Polyethylene, positive pressure single acting hand pumps designed for handling corrosive fluids are available in 24, 30 and 36-inch barrels from Bel-Art Products, 4917 Murphy Place, West New York, N.J. All working parts are made of polyethylene.

•

Alloy Steel Products Co., Inc., Linden, N.J. has been purchased by Walworth Company and will be operated as an independent subsidiary of the company retaining present management, employees and policy. Walworth also has acquired recently M & H Valve and Fittings Company of Anniston, Ala. and Southwest Fabricating and Welding Co., Inc., Houston.

•

Ultrasonic vibrations on the order of 20,000 cycles per second can be produced now with low cost high frequency rotating generators ranging in size from two to 150 kilowatts, according to Acoustica Associates, Inc., Glenwood Landing, L.I., N.Y. Multiple transducers can be energized by these generators for improved cleaning, grinding and other applications.

•

Ice Skating Rinks, a special report on construction and maintenance has been issued by A. M. Byers Co., Pittsburgh, Pa. in an illustrated 32-page and cover booklet. The report shows that not one of thirteen rinks originally piped with steel operated for more than seven years without pipe failure. Almost all of the steel piped rinks have been repiped at least once. Of the 12 rinks in which Wrought iron piping was used failures have occurred in three cases, with no failures in less than nine years and an average life before failure of 16 years. Details of rink construction are shown.

Titanium Progress Report No. 2, published by Pigments Department, E. I. DuPont de Nemours & Co., Ltd., Wilmington 98 Del. shows some of the recently developed commercial uses for titanium in the chemical, commercial aircraft and food processing industry.

•

Kaiser Aluminum & Chemical Corp. has purchased the government owned aluminum extrusion plant at Halethorpe, Md.

which it has been operating under lease since 1951. The plant is now capable of producing 24 million pounds of extrusions annually.

•

Aluminizing the dome and walls of sulfuric acid converters prevents corrosion of these surfaces and consequent smothering of the vanadium catalyst, according to Emjay Maintenance Engineers, 327 Union Ave., Rutherford, N.J.

NEW PRODUCTS

(Continued From Page 89)

Dravo Corporation has started construction of a new facility for centralized research. The T-shaped masonry Dravo Research Center, expected to cost $400,-000, will be completed in three years.

•

Endcor 50, a chemical treatment designed to control corrosion of petroleum production equipment is a strongly polartype organic corrosion inhibitor incorporated in a liquid carrier dispersible in water but insoluble in oil. The inhibitor is introduced into the annulus of a producing well where it penetrates the oil layer to the brine. It is preferentially adsorbed on metal surfaces from the brine. Treatment quantity is based on brine content of produced fluid, normally at the rate of 50 ppm but never less than 10 ppm of total fluid. Manufacturers claim efficiencies in some tests as high as 98 percent, measured by wellhead tests. More data are available in Bulletin 50, available on request from Dearborn Chemical Company, Merchandise Mart Plaza, Chicago 54, Ill.

•

Inco Development and Research Division's Central Atlantic Coast Technical Field Section headquarters is now in the Abington Bldg., Abington, Pa.

•

Seal-Kote, a one-coat vinyl all-purpose paint has been developed by The Wooster Sealkote Co., Wooster, Ohio. Manufacturers claim it can be used on wet or dry surfaces, including masonry, where it prevents further water penetration.

•

Corrosion-Proof Battery Oil Cup Terminals made by Jano Machine Co., 836 North Broadway, Escondido, Cal. are said to eliminate corrosion of battery terminals.

•

Atomic fueled power stations may generate electricity for Distant Early Warning radar stations to be built by the United States across the Canadian arctic.

•

Sea-Rite Salt, a simulated sea salt mix containing elements found in natural sea salt in quantities greater than 0.0004 percent is available from Lake Products Co., Inc., 1252 Grover Road, St. Louis 23 (LeMay) Mo. It is available in 100-lb. fiber drums.

•

Clear Coating-CH 64, a water white butyrate protective lacquer has protected the original bright surface of an aluminum truck trailer during a 16-month's test. Portions of the trailer left uncoated for comparison were pitted and dulled. Application follows a solvent wash without primer. Adhesion proved good even in dented areas. Other tests also showed improved washup time. The transparent coating does not require preliminary masking, is applied readily by standard spray equipment and gives substantial protection even with one coat. The material was developed jointly by Egyptian Lacquer Manufacturing Co., South Kearney, N.J. and Lafayette, Ind. and Eastman Chemical Products, Inc., Kingsport, Tenn.

•

Paper that will freely permit passage of air but resist passage of oil, water or other liquids has been developed by Riegel Paper Corp., 260 Madison Ave., New York 16, N.Y. The company is seeking suggestions as to potential uses of the new paper.

•

Micro-Switch, Freeport, Ill. has a sealed, cylindrical switch, one inch in diameter by two inches high which is filled with inert gas under pressure. The switch, designed for use in airplanes, has operating characteristics independent of weather and atmospheric environment.

•

Gamma Radiographic techniques permitted examination of as many as 50 valves at a time by Isotope Products, Buffalo, N.Y. The company radiographed more than 700 valves of various sizes to be used in the heavy water system of a new NRU reactor at Welland, Canada.

•

Corrosion Resistant, precipitation hardenable stainless steel alloys designed PH55A, PH55B, PH55C and PH20 developed by Cooper Ally Corp., Hillside, N.J. are described in the July 1955 CA Newscast, a periodical available from the company.

•

Lignite Tars, produced as a by-product of the carbonization of lignite at the Aluminum Company of America's plant near Rockdale, Texas are a new raw material for the chemical industry. Research is being conducted by Battelle Memorial Institute on 16,000 pounds of lignite tar daily produced by a prototype carbonizer.

•

Bakelite epoxy resins used to impregnate electrical coils, protect them against vibration, wide ranges of temperature, and most liquids and gases in the environment. They are recommended for uses involving water.

•

Type 20 and Hastelloy C are now being used to fabricate the Eco All-Chem stainless steel positive displacement process pump. Eco Engineering Co., Newark, N.J. is manufacturer.

•

Air Motors made by The Bellows Company, 222 W. Market St., Akron, Ohio are suggested for use in hazardous locations and for precise control of manufacturing operations. They are described in Bulletin ML-3 available from J. G. McComb.

•

Instrumentation fittings of unplasticized PVC are now available from Tube Turns Plastics, Inc. Louisville, Ky. Fittings and tubing, available in ¼ and ⅜-inch sizes make possible assembly of piping systems without tools and make possible pneumatic instrumentation in many places where electrical circuits heretofore were considered more suitable. Maximum working pressure is 150 psi and temperature 75 F.

•

Geodesic plastic sphere, 55 feet in diameter, was molded in 363 parts by Lunn Laminates, Inc., Huntington Station, L.I., N.Y. The structure, designed for an unspecified military use, can withstand wind velocities up to 200 mph.

•

Speco, Inc., 7308 Associate Ave., Cleveland 9, Ohio has added an inhibitor to its Ice Rem snow melting pellets designed to improve storage life and reduce corrosion of automobiles and other metal structures affected by the produced brine. The material of unspecified nature is reported to consist principally of an "essential" oil.

•

Plasticizer 84, an octyl butyl pthalate for use in nitrocellulose formulations has been developed by Eastman Chemical Products.

•

Alvin Products, Inc., Worcester, Mass. is marketing an aluminum-based compound called "Lab-Metal." Applied in paste form to metal, wood, plaster, glass or plastic, it may be machined, chiseled, sawed and sanded. It is unaffected by mild acids, alcohols, toluene, ether, petroleum and petroleum solvents.

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Dynel Safety Bags to enclose laboratory

NEW PRODUCTS

(Continued From Page 90)

pressure bottles in boiling water baths are available from Flaherty Filter Fabrics.

Polyethylene containers made by Austin Industries, Inc., Marlboro, Mass. are recommended for packaging of metal parts to protect them against the environment. Transparency of film permits easy identification of contents.

DuPont's Electrochemical Department will install a multimillion dollar addition to the plant now under construction near Antioch, Cal. for production of sodium, ethyl chloride, trichlorethylene and perchlorethylene.

People and Pipe, a 52-page history of American Cast Iron Pipe Company of Birmingham, Ala. will recount the 50-year history of the company. It is being issued as part of the firm's Golden Anniversary Celebration, the founding having been on October 5, 1905. American Cast Iron Pipe Company has pioneered in making 16-foot lengths, concrete linings and most recent and important, the Mono-Cast centrifugal process. The company also makes centrally spun steel tubes and industrial alloy iron castings.

Beryllium Copper Tubing is used for aircraft antenna by Aircraft Radio Corp., Boonton, N.J. The tubing is made by Superior Tube Company, Norristown, Pa.

Zircaloy 2, a new zirconium alloy developed by Westinghouse Electric Corp., is reputed to be so resistant to the corrosive action of high-temperature, high-pressure water in nuclear reactors that wastage in a year's time was only one-ten thousandths of an inch. This is reported by Armour Research Foundation's Industrial Research Newsletter.

Molykote Type BR2 is described in Bulletin 101 available from Alpha Molykote Corp., 65 Hartford Ave., Stamford, Conn. The lithium base grease is designed for extreme bearing pressures.

Porcelain Enamel can be applied in a wide variety or matte and glossy colors to 50-inch aluminum foil by Keasbey Corp., an affiliate of General Ceramics Corp., Keasbey, N.J.

Ruf-Nek paste, designed for application to any metal whose melting point is higher than the paste (1850 F) consists of powdered hardfacing alloy in a water solution. After application to the metal surface it can be cured with either gas flame or induction heating, according to thickness of base metal.

Chromizing applications are described in a 4-page bulletin available from Chromalloy Corp., 109 West 64th St., New York 23, N.Y. Improved wear and corrosion resistance are imparted by the process, which is said to diffuse chromium into the metal surface at high temperatures. Ductile cases from 0.001 to 0.003-inch on low carbon steel, among other uses, permit using this material in some applications where 400 series stainless would be indicated, manufacturers claim.

PERSONALS

Fred M. McConnell is now sales engineer with Service Coating Corp., 217 Lagoon Ave., Wilmington, Del. He was NACE Western Region membership chairman in 1954.

•

Clarence E. Larson has been appointed vice-president in charge of research by National Carbon Company, a Division of Union Carbide and Carbon Corp. Dr. Larson formerly was director of Oak Ridge National Laboratory, operated by Union Carbide for the Atomic Energy Commission. His headquarters will be at Cleveland at the company's new research laboratory now under construction. Dr. Larson recently returned from Geneva, Switzerland where he was an official delegate to the United Nations Conference on Peaceful Uses of Atomic Energy.

•

Douglas B. Fraser has been named manager of the Cincinnati plant of Alco Products, Inc. The plant manufactures pipe to augment the company's line of process equipment.

•

John E. Searcy, Jr., has been appointed vice-president in charge of engineering of Corrosion Control, Inc., Tulsa, Okla. The new firm will offer corrosion control engineering service in connection with the operation of on and offshore pipelines, oil production and refining equipment, cables, heat exchange and marine equipment.

Theron S. (Ted) Bushnell has been named Midwest District manager of Tube Turns Plastics, Inc., Louisville, Ky. His headquarters will be in Chicago.

•

Leonard Smiley will be manager of technical coordination in the Atomic Energy Division of Sylvania Electric Products, Inc.

•

H. R. Crittenden, 9 South Clinton St., Chicago has been named agent for Vanton Pump & Equipment Corp., Hillside, N.J. for northern Illinois.

Clifford A. Hampel has joined Fansteel Metallurgical Corp. North Chicago, Ill. as manager of chemical equipment division to be responsible for engineering, design and sale of products to the chemical process industries, including acid-proof tantalum equipment.

•

Lynn C. Edgar has been appointed sales manager of Tube-Kote, Inc. to supervise sales engineers in a seven-state Southwestern area and personally service Tube-Kote customers in the North Texas region.

•

Dominick Labino has been appointed vice-president and Director of Research of the L.O.F. Glass Fibers Co. He has been with the company since 1947 and was the first man to synthesize quartz in micro-fiber form, an important high temperature insulation material. **Ellsworth Smith,** formerly new product manager in the general engineering department has been named technical director. Their headquarters will be in the company's new research center planned for construction at Waterville, Ohio.

•

Paul Bachman, formerly a director of NACE and recently vice-president of Davison Chemical Company, has been elected vice-president and Director of Research and Development of Koppers Co., Inc. He will guide the research and development functions of the company, with responsibility for development of research policies and objectives. **Dr. E. W. Volkmann** will continue as manager of Koppers Research Department.

•

J. L. Stewart has been appointed assistant regional manager, Pumps, in the Houston office of Byron Jackson Div., Borg-Warner Corp.

•

J. L. Canwell, vice-president of the Pennsylvania Railroad Co., New York has been elected president of the American Standards Association.

•

James B. Carse has been named marketing manager of H. M. Harper Company, Morton Grove, Ill.

•

Roy B. McCauley, Jr., has been appointed chairman of the department of welding engineering of Ohio State University, Columbus.

•

Erwin J. Campbell has been named supervisor of process research, Research and Development Dept., Acheson Colloids Co., Port Huron, Mich.

Indian Institute to Meet

The Ninth Annual General Meeting of the Institute will be held in Calcutta on December 20-22, 1955. The Second Educational Lecture Series on the "Mechanical and Physical Properties of Steel" will be held in conjunction with the meeting.

Corrosion Abstracts

Index to
CORROSION ABSTRACTS

1. GENERAL

1.6 Books

1.6, 3.1

Korrosion under Korrosionshutz. (In German). FRITZ TODT, Editor. Book, 1102 pp., 1955. Walter de Gruyter & Co., Genthinerstr. 13, Berlin W 35, Germany.

A comprehensive volume covering theoretical and practical aspects of the corrosion of metals in most environments. Each of the several subdivisions of the volume has its own editor. There are hundreds of photographs, diagrams, charts and tables of data. Each subdivision is liberally referenced. There is a 70-page alphabetical subject index.

For the corrosion worker with a knowledge of German this book should prove a useful reference. The wealth of worldwide literature references alone makes it valuable.   9215

1.7 Organized Studies of Corrosion

1.7.1

Department of Metallurgy at the University of Cambridge. *Metal Treatment*, **21**, No. 104, 215-223 (1954) May.

History of research at Cambridge; courses provided; laboratories and equipment for teaching and research; researches now in progress (on molten metals; structures and properties of steels and copper and effect of coatings; fatigue;

electrolytic polishing and electrodeposition; corrosion; miscellaneous).—BNF.
9142

2. TESTING

2.1 General

2.1.1, 1.7.1

Italian Standardization in the Field of "Corrosion of Metallic Materials." (In Italian). *Metallurgia italiana*, **46**, special supplement to No. 5, 141 (1954) May.
General program.—BTR.   9160

2.1.1, 3.2.3

Corrosion of Metals: Corrosion Rates Under Uniform Attack—DIN 50901. P. MELCHIOR AND W. WIEDERHOLT. *Werkstoffe u. Korrosion*, **5**, No. 5, 178-182 (1954).

After a short introduction, this new German standard is given in full. It lays down notation and units for the quantities used in metallic-corrosion studies. The standard, which is in six sections, is a revision of the previous German standard DIN 4851 of October, 1937.—MA.
9146

2.2 On Location Tests

2.2.1, 2.3.1, 1.7.1, 6.4.2

Methods of Corrosion Testing at the Instituto Sperimentale dei Metalli Leggeri. (In Italian). G. LUFT. *Metallurgia italiana*, **46**, special suplement to No. 5, 122-124; disc., 124 (1954) May.

Methods estimate corrosion resistance of aluminum alloys. Photographs, diagrams. 12 references.—BTR.   9156

2.2.2, 5.4.5

Performances of Finishes with Different White Pigment Combinations at Five Localities of Varying Climatic Conditions. H. GERET. *Schweiz. Archiv,* **20**, No. 1, 18-24 (1954).

Exposure tests over a period of 2 years, with paints made up to a pigment volume concentration of 20-25 percent without any extenders using linseed stand oil or an alkyd resin as a medium. The effect of climatic factors was assessed in terms of loss of gloss, chalking and change in appearance of the paint films (cracking and checking). Test panels exposed to an Alpine climate showed hardly any paint breakdown, whereas the atmospheric pollution in an industrial town caused severe disruption.—EL.   9236

2.2.2, 6.2.1, 1.7.1, 5.3.2

Report of (ASTM) Sub-Committee XIV on Inspection of Black and Galvanized Sheets. C. P. LARRABEE. Am. Soc. Testing Materials Preprint No. 3, 1954, 5-17.

The results of exposure tests on black and galvanized steel sheet that have been carried out continuously since 1916 are given in detail. Marine, industrial and rural atmospheres are included. In all environments steels or wrought iron with at least 0.2 percent copper have approximately twice the life of those containing < 0.02 percent copper. The corrosiveness of the atmospheres varies more than the corrosion-resistance of the sheets tested. For galvanized sheet, the time for rusting to begin α the weight of the zinc coating. Although the composition of the base metals had no measurable effect on the life of the coating, it was the major factor determining the first perforation of the coating. Corrosion rate of zinc depends more on the type of atmosphere than does that of the steel sheet.—MA.   9151

2.3 Laboratory Methods and Tests

2.3.4

Simultaneous Volumetric Determination of Copper, Iron, Lead and Zinc in Copper-Base Alloys. (In German). J. KINNUNEN AND B. WENNERSTRAND. *Metallurgia,* **50**, No. 299, 149-150 (1954) Sept.

A procedure based partly on known methods permits determination of copper, lead and zinc in leaded brass from same initial weight, or without use of balance. Copper, lead and zinc in gunmetal can be determined in 15 min.; tin by difference or separately. An alternative method is put forward for low lead and zinc contents.—BNF.   9164

2.3.6, 2.6, 2.3.9

Recent Developments on Apparatus to Prepare Polished Micro-Sections and for Metallographic Examination. (In German). RICHARD PUSCH. *Stahl und Eisen,* **75**, No. 6, 335-345 (1955) March 24.

Communication from the Mannesmann-Forschungsinstitut. Report No. 939 of the Committee for Materials of the Verein Deutscher Eisenhuttenleute, Survey on the development of apparatus for the preparation and microscopic examination of metallographic specimens during the last two decades approximately. Methods of illumination, optical equipment, technique of obtaining photo-micrographs, additional equipment and development of the design of the metallographic microscope.—SE.   9221

2.3.7

Comparative Investigations of Thickness Testing Methods. Parts I, II. H. BARGHOORN. *Metalloberflache,* **7**, Nos. 2, 3, 20B-25B, 36B-38B (1955).

Part I. The Mesle cord, direct measurement, optical, magnetic and electric methods of determining coating thicknesses are discussed.

Part II. Determination of coating thickness by direct weighing, by calculation from electrochemical equivalent and by wet and dry tests, are briefly described. The most accurate results are obtained by the Ultraoptimeter, microscopic methods and direct weighing in that order. Other non-destructive methods, e.g., magnetic tests are judged inaccurate up to 0.8 mil, jet and drop tests are fairly accurate ($\pm$ 10%) irrespective of deposit thickness.—EL.   9233

2.3.7, 3.5.8, 6.4.2, 2.3.4

Inter- and Transcrystalline Corrosion and the Testing Thereof. (In German). F. C. ALTHOF. *Metall,* **9**, No. 3/4, 110-120 (1955) February.

In the introductory part a distinction is made between transcrystalline and intercrystalline corrosion. The former is always largely promoted by applied mechanical stress. The latter, may appear either as a result of stress or as a pure disintegration along the grain boundaries. However, in the case of light metals it is difficult to establish an *a priori* difference and usually both processes are termed stress corrosion. The different ways to apply mechanical stresses are described, in this respect the method of testing light metals does not differ from that of others. The chemical procedure, for testing aluminum and magnesium alloys is usually done under simulated practical conditions, i.e. in contact with water, or water and 3 percent sodium chloride and 0.1 percent sulfuric acid, or salt solutions and potassium chromate, or hydrogen peroxide—sodium chromate, artificial seawater or by simple exposure to natural weather conditions. The fact that small changes in the variables affect the results very considerably makes it difficult to establish correlation between chemical agent and alloy.—ALL.   9225

2.3.7, 5.3.2

Hardness Measurements on Electrodeposited Coatings. Part II. (In German). A. KEIL AND E. MERKLE. *Metalloberflache,* Sec. A, **8**, No. 9, A129-A131 (1954) September.

Two examples. One (on rhodium coatings) confirms the earlier view of a sharply-defined limit for the permissible depth of impression of the diamond, if there is a great difference in hardness between coating and basis metal. In the other, it is shown how Durimet hardness tests can be used to investigate the relative throwing power of the components of alloy plating baths. In the present tests a silver-lead-cyanide-tartrate bath was used: alloys of varying lead content were deposited at different parts of a brass cathode. Durimet tester, load 15-300g, is intermediate between micro- and macrohardness.—BNF.   9101

2.3.7, 5.4.5

An Instrument for Measuring the Chip Resistance of Paints. E. P. BRIGHTWELL. *ASTM Bull.,* No. 200, 53-55 (1954).

A compact portable instrument is described to test chip resistance in paints consisting of a rod holding a plunger with a hardened steel hand which strikes the paint coating. The spring tension on the rod is variable and the rod is relieved by a trigger mechanism. A standard deviation is less than 3 percent.—EL.   9211

2.3.7, 5.4.5

Tritium Determines Moisture Gradient in Attached Protective Coatings. G. D. CALKINS, M. POBERESKIN, V. E. YOUNG AND L. J. NOWACKI. *Nucleonics,* **13**, 76-77 (1955) February.

Exposing varnished specimens to tritated water vapor permits *in situ* evaluation. Graphs, table, diagram. 6 references. —BTR.   9214

2.3.7, 5.4.5, 6.4.2. 7.5.2

Control of Porosity of Varnish Films Applied to Aluminium Food Containers. (In Italian). G. LUFT AND T. FEDERIGHI. *Alluminio,* **23**, No. 4, 391-398 (1954).

An electrical method of testing the porosity of the protective varnish film on aluminum food containers is described. Using a modification of the apparatus described by Mehnert [*Arch. Metallkunde,* **2**, 140 (1948)], the porosity of the film can be determined from its electrical resistance. 106 aluminum containers were examined over periods up to 80 days. The method permits the quality control of containers subjected to mechanical loads and the degree of porosity can be expressed in straightforward numerical terms.—MA.   9171

2.3.7, 5.4.5

The Adhesion of Paints to Metallic Surfaces. C. D. LAWRENCE. *Electroplating and Metal Finishing,* **7**, No. 12, 461-465 (1954) December; *ibid.,* **8**, No. 1, 14-18 (1955) January.

Importance of adhesion of organic coatings to metals is discussed. Mechanism of adhesion is dealt with and the methods used to test adhesion are described in detail. Direct measurement of adhesion is carried out by methods of Schmidt; Paint & Varnish Production Club; Courtney & Wakefield; Moses & Witt; and Malloy, Soller and Roberts. Scraping or scratch tests include a method devised by New York Paint & Varnish Prod. Club, a method using the Interchemical Adherometer and various scratch tests. Two impact tests detailed in Ministry of Defence Specification are described as well as deformation tests including the bend and Erichsen tests. Also discussed are special tests for underwater paints; choice of testing method; and the various factors influencing adhesion, including cleaning and pre-treatment, wash primers and paint systems. Diagrams, illustration and 13 references.—INCO.   9159

2.3.7, 6.6.6, 6.7.2

High-Temperature Testing Techniques for Brittle Refractory Materials. J. J. GANGLER. *J. Am. Ceram. Soc.,* **37**, No. 9, 439-444 (1954) Sept.

Techniques developed at NACA Lewis Flight Propulsion Laboratory for testing ceramics, cermets, etc. Stress-rupture and creep testing, single- and multiple-cycle thermal shock tests, testing as blades in gas turbine engines.—BNF.   9253

2.3.9, 2.3.6

Electron-Optical Methods in Constitutional Metallurgy. J. W. MENTER. *J. Inst. Metals,* **83**, 185-192 (1954) Dec.

The use of electron diffraction makes it possible to determine the crystallographic nature and chemical identity of surface constituents. The value of elec-

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- Efficiency Guaranteed
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Single and 3 phase models. Regular or external adjusting types. Unit easily removed for inspection. Quick change wider range voltage adjustments and other features same as self-cooled model. Also available in *EXPLOSION-PROOF* single and three phase models for *HAZARDOUS LOCATIONS*. Basically the same as all oil-immersed units. Extra deep case. Unit submerges 6 to 7 inches under oil. Explosion-proof fittings for D.C. leads. Meter switches and A.C. line enclosed in explosion-proof housing.

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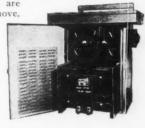
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Homco and Barada and Page Backfills
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tron diffraction is enhanced when used in combination with electron-microscopic methods either in transmission or reflection.—NSA. 9174

2.3.9, 2.3.6
A New Sample Stand for Spectrographic Analysis. (In German). W. KOCHLER. *Spectrochim. Acta*, 6, No. 3, 223-227 (1954) May.

Stand for analysis of small areas (down to 0.2 mm), fitted with binocular microscope to observe counter-electrode and area examined; applied to analysis of inclusions and intermetallics.—BNF.
9134

2.3.9, 7.1
Radioactive Isotopes for Measuring Piston Ring Wear. J. H. DETERDING AND A. DYSON. *Engineer*, 198, 442-445 (1954) October 1.

Normal piston rings are irradiated in the Harwell pile, then after about four weeks are fitted to engines and used for wear tests, by observing the radio-activity of the oil. Results with chromium-plated rings are given.—BNF. 9264

2.4 Instrumentation

2.4.2, 6.4.2, 2.3.2
Aluminum Salt Spray Chamber. H. P. GODARD. *Chem. Can.*, 6, No. 11, 22 (1954) November.

A case history is given of a painted aluminum salt spray chamber constructed in 1946 which confirms the good corrosion performance of aluminum and its suitability as a construction material for salt spray testing equipment. The 375 cu. ft. salt spray chamber was constructed at Aluminium Laboratories Limited, Kingston, using one-quarter inch plate in Alcan 3S aluminum alloy. The interior of the chamber was painted after construction as follows: 1) Degreased by swabbing with carbon tetrachloride. 2) Air-dried. 3) Hosed down with hot water. 4) Washed with phosphoric acid-alcohol solution (butyl alcohol—40 volumes, isopropyl alcohol—30 volumes, 85 percent phosphoric acid—10 volumes, water—20 volumes). 5) Primed with one coat of zinc chromate primer. 6) Painted with two coats of aluminum paint containing two pounds Alpaste per gallon of glyceryl phthalate spar varnish with 3 percent xylene by volume as thinner. The chamber was operated intermittently for eight years using mostly 3.5 percent salt spray at 95 F. At the end of this period there was no breakdown of the paint system or corrosion of the aluminum.—ALL. 9241

2.4.3
Accuracy of Measurements of Corrosion Damage and of Wall Thickness by the Ultrasonic Method. A. LUTSCH. *Z. Ver. Deut. Ing.*, 96, No. 23, 773-777 (1954) August 11.

Determination of location and extent of corrosion damage and measurement of wall thickness of e.g. boilers and boiler tubes, where only one side of the wall is accessible, by use of the pulse-reflection method. General remarks on testing for surface corrosion. Detection of localized limited surface corrosion. Detection of extensive surface corrosion; "electronic magnification" (delayed sweep). Measuring wall thickness using the standard setting and using the delayed sweep setting, respectively; results of tests (Table 2). Measuring thin plates. Examples from actual practice illustrating the technique of measuring defects of various sizes.

Accuracy of results attainable; importance of correct interpretaton of the oscilloscope pattern. Translation available: Henry Brutcher, P. O. Box 157, Altadena, California. 9173

2.4.3
Recent Advances in Ultrasonic Non-Destructive Testing. J. KRAUTKRAMER. *Z. Metallkunde*, 45, No. 4, 154-157 (1954).

Improvements of pulse-echo technique. Simplified operation of apparatus and simplified interpretation of results; use of "depth transducer head" with built-in sensitivity regulator. "Defect location rule" for the testing of welds (Fig. 1). "Section thickness measuring attachment" (Figs. 2 and 3) for determining section thicknesses of less than 5/16-inch. Increased testing speeds (and reduced testing cost) by improved acoustic coupling. Testing of tube and pipe stock (Fig. 4). "Shielded" transducer to minimize transducer wear. Transducer head design enabling the testing of more intricately shaped parts. Application of pulse-echo technique to metallurgical problems; "Interferometer" attachment for measuring the velocity of sound, and how this attachment operates. Translation available: Henry Brutcher, P. O. Box 157, Altadena, California. 9167

2.4.3, 7.2
Detection of Discontinuities in Metal Tubes by Induced Electric Currents. (In French). G. GAUTHIER. *Rev. Met.*, 51, No. 8, 537-540 (1954) August.

Investigation of 70 copper-30 nickel tubes at a frequency of 7000 cycles. Author was able to detect small internal cracks but size indication was not very reliable.—BNF. 9252

2.6 Preparation and Cleaning of Specimens

2.6, 2.3.7
Treatment of Tension Test Specimens for Fixing in Testing Machine. H. KRENCHEL. *ASTM Bull.*, No. 200, 44-46 (1954) Sept.

Describes coatings that can be applied to the ends of high-tensile steel wires to facilitate gripping in the jaws of tensile or fatigue testing machines. Various resins used either alone or reinforced with soft iron wire or carborundum powder.—BNF. 9170

3. CHARACTERISTIC CORROSION PHENOMENA

3.2 Forms

3.2.2, 1.1
Note on "Inverted Relief" in Photographic Illustrations—A Technical Note. NEIL S. DEMPSTER. *Corrosion*, 11, No. 7, 312t-314t (1955) July.

The author points to errors in the orientation of photographs illustrating pitting or blistering forms of corrosion which result in incorrect relief perception by the reader. That is, pits appear to be blisters and vice versa. He suggests the reason for this misconception is incorrect orientation of the illustrations with respect to the location of the shadow. It is recommended further that the general policy be adopted of photographing specimens illustrating pitting and blistering phenomena so that the shadow falls toward the bottom of the paper. 9124

3.2.2, 4.6.2, 3.8.4, 5.8.2
Filiform Corrosion Products on Iron Immersed in Brine. P. F. THOMPSON AND K. F. LORKING. *Corrosion*, 11, No. 7, 309t-311t (1955) July.

A new type of filiform corrosion pustule has been observed on steel test specimens immersed in a commercial refrigerating brine containing chromate as a corrosion inhibitor. These filaments were secondary corrosion products growing from primary hemispherical pustules on the metal surface. The mechanism of the growth of the filaments is discussed.
9190

3.2.2, 6.2.5
How to Control Hydrogen Embrittlement in 12% Chrome Steels. A. E. DURKIN. Gen. Elec. Co. *Iron Age*, 174, No. 24, 154-156 (1954) December 9.

The effect of various media in producing hydrogen embrittlement, the effect of different factory heat treatments on the susceptibility of 12 percent chromium steel (with 0.5 percent nickel) to hydrogen, the effect of the hydrogen on tensile strength, elongation and endurance of the steel and the effect of acid and caustic solutions on specific hardness were among the problems investigated. Results indicated that the harder the material, the more susceptible it is to hydrogen embrittlement. Materials tempered in the 1000 F range show less susceptibility than those tempered in a lower range. Organic protective coatings help by preventing corrosion, leaving no hydrogen available to diffuse into the metal. Acid solutions are more severe than caustic solutions and attack the metal, causing stress risers. Elongation is influenced by hydrogen embrittlement. An analysis of 12 percent chromium steels is tabulated and experimental data are shown in graphs. 3 references.—INCO. 9261

3.2.2, 6.2.5, 3.6.5
Contribution to the Problem of Intergranular Corrosion of Austenitic Chromium-Nickel Steel. (In German). ERWIN BRAUNS AND GUNTHER PIER. *Stahl und Eisen*, 75, No. 9, 579-586 (1955) May 5.

Plotting of "current-density-potential" curves of an unstabilized stainless steel containing 0.08 percent carbon, 17.8 percent chromium and 7.6 percent nickel after quenching and reheating to 650 C for up to 192 hours. Occurrence of two activation potentials being due to a different activation potential of grain boundary and grain surface. Relation between the current-density-potential curve and the mode of action of boiling copper sulfate-sulfuric acid solutions. Effect of the Redox potential on the intergranular corrosion and effects being decisive for the adjustment of the Redox potential of the copper sulfate-sulfuric acid solution.—SE. 9213

3.2.2, 6.3.15, 1.6
The Effects of Hydrogen on the Mechanical Properties of Titanium and Titanium Alloys. Summary Report. G. A. LENNING, C. M. CRAIGHEAD, AND ROBERT I. JAFFEE. Battelle Memorial Inst. (Contract DA-33-019-ORD-938.) July 31, 1954, 100 pp.

Results are given on the effect of notches, testing speed and testing temperature on hydrogen embrittlement of high-purity titanium, commercial purity titanium (A-55) and the commercial 8 percent manganese alloy (C-110 M). The effect of hydrogen on the microstructure and mechanical properties of alphabeta and beta titanum—molybdenum alloys is presented. Hydrogen pickup of A-55 and

C-110 M dride and ling was of hydro A-55 and (auth.)—

3.2.2, 7.7
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3.4.7, 6.2.
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C-110 M totanium alloys in sodium hydride and Virgo descaling and acid pickling was also investigated. The removal of hydrogen by vacuum annealing of A-55 and C-110 M titanium was studied. (auth).—NSA.   9161

3.2.2, 7.7
Abnormal Parasitic Crystals (Whiskers) on Metals Having a Protective (Metallic) Coating. (In French). E. GEFFROY. *Metaux, Corrosion—Industries*, **29**, No. 345, 212-215 (1954) May.

Cases of whisker growth on metallic coatings (zinc, cadmium or tin) on metals and non-metals in transformer equipment.—BNF.   9242

3.4 Chemical Effects

3.4.7, 6.2.2
Dependence of Iron Corrosion Velocity on the pH of KCl Salt Solution. (In Russian). L. K. LEPIN' AND A. IA. VAIVADE. *J. Phys. Chem., USSR* (Zhurnal Fizicheskoi Khimii), **28**, No. 3, 435-439 (1954) March.

Experiments with pH values from 3 to 9. Table, graph. 10 references.—BTR.   9158

3.5 Physical and Mechanical Effects

3.5.8
Nature of Fracture in the Plastic Deformation of Metals. (In Russian). S. I. GUBKIN AND L. A. RAPOPORT. *Doklady Akad. Nauk SSSR*, **94**, No. 4, 685-688 (1954) February 1.

Discusses the part played by localized plastic deformation and inhomogeneities. —BNF.   9248

3.5.8, 3.5.9, 6.3.3
Investigation of Effect of Notches on Elevated-Temperature Fatigue Strength of N-155 Alloy. C. A. HOFFMAN. National Advisory Comm. Aeronaut., RM E53L31a, April 26, 1954, 8 pp.

Studies were made at 1350 and 1500 F in completely reversed bending. Results on relatively few specimens indicated that: notches reduced fatigue strength at 1350 F by approximately 34—40 percent and at 1500 F by approximately 30—37 percent over the range of 3-150 hours; and the notch sensitivity in fatigue under conditions of completely reversed bending at 1350 and 1500 F was considerably less than that predicted for static bending under elastic conditions.—INCO.   9185

3.5.8, 3.8.4, 6.3.19
The Cleavage Fracture of Pure Polycrystalline Zinc in Tension. G. W. GREENWOOD AND A. G. QUARRELL. *J. Inst. Metals*, **82**, No. 12, 551-560 (1954) August.

The effects of grain-size, temperature, strain rate and plastic deformation on the type of fracture and fracture stress were investigated. The true fracture stress was found to be inversely proportional to the square root of the mean grain diameter at —196 C and the relationship was valied at higher temperatures after corrections for the effect of deformation and the temperature. An activation enery for elongation to fracture was determined. It is concluded that a dislocation theory can be developed to account for the build-up of large internal stresses from which cracks leading to cleavage can result. 18 references.—ZDA.   9243

3.5.8, 6.4.2
Fatigue Phenomena in High-Strength Aluminium Alloys. R. F. HANSTOCK. *J. Inst. Metals*, **83**, No. 1, 11-15 (1954) Sept.

Increase in damping capacity preceding fatigue failure of aluminum alloys L 65 and DTD 683 is associated with precipitate instability. Localized bands of precipitation in DTD 683 give rise to fatigue cracks. Fatigue strength depends on magnitude of stress required to initiate precipitation and on strength of over-precipitated region.—BNF.   9186

3.5.8, 6.4.2
Corrosion-Fatigue Properties of an Aluminium-Magnesium-Silicon Alloy in the Unprotected, Anodized, and Painted Conditions. N. P. INGLIS AND E. C. LARKE. *J. Inst. Metals*, **83**, Pt. 4, 117-120 (1954) Dec.

The endurance strength of a fully heat-treated aluminum alloy of the H10 type has been determined in air and when subject to the action of distilled water, ordinary tap-water and a 3 percent sodium chloride solution. The endurance strength of the alloy was much reduced in the presence of these liquids, the corrosion-fatigue strength in Birmingham or London tap-water being about half that in air, while the corrosion-fatigue strength in the salt solution was only 25 percent of the fatigue strength in air. Anodizing afforded an appreciable measure of protection against corrosion-fatigue effects, although the fatigue strength in air of the anodized metal was rather lower than that of the unprotected metal. Painting in accordance with a carefully specified schedule gave extremely effective protection even under the most severe corrosion-fatigue conditions, the fatigue strength of the painted material in the salt solution being rather better than that of the unprotected material tested in air. (auth).—MA.   9177

3.5,9, 1.7.1
High Temperature Corrosion Data: A Compilation by Technical Unit Committee T-5B on High Temperature Corrosion. JOHN J. HALBIG, Chairman. National Association of Corrosion Engineers Pubn. No. 55-6; *Corrosion*, **11**, No. 5, 241t-245t (1955) May.

The behavior of 31 materials ranging from cast iron to lead, including a number of stainless steels and high alloys subjected to temperatures over 400 F is tabulated. Data are derived from Shell Development Company's Corrosion Data Survey (1948), among other sources. Corrosion rates are indicated as low, moderate or high versus specific temperatures. Additional data are solicited by the compiling committee.   9192

3.6 Electrochemical Effects

3.6.8, 4.7
The Hydrogen Overvoltage on Mercury in Alkaline Solutions. Z. A. IOFA. *J. Phys. Chem., USSR* (Zhur. Fiz. Khim.), **28**, No. 6, 1163-1165 (1954).

Iofa discusses his previous work [Kaptsan and Iofa, *Ibid.*, **26**, 193, 201 (1952)] and the controversial paper of Volkov-[*ibid.*, **27**, 195 (1953)] on the hydrogen overvoltage on mercury in alkaline solutions. It is pointed out that the direct measurement of the overvoltage on mercury in alkaline solution is usually impossible owing to the loss of current caused by amalgam formation. This difficulty is avoided by using $N(CH_3)_4OH$

solutions, in which case the polarization curves $\eta/\log$ current density (where η is the hydrogen overpotential) can be determined over a wide range of current density. Such a curve for $1N$-$N(CH_3)_4OH$ solution is shown and discussed.—MA.   9149

3.6.8, 5.8.3, 4.7
Adsorption of Surface-Active Agents and the Hydrogen Overvoltage on the Surface of Solid Mercury. (In Russian). V. L. KHEIFETS AND B. S. KRASIKOV. *Doklady Akad. Nauk SSSR*, **94**, No. 3, 517-518 (1954).

The capacity of the double layer in solutions of 2N-sulfuric acid in 80 percent ethanol, with and without additions of nonanol, was measured as a function of the electrode potential with a mercury electrode at —38 and —41 C. The cathode branches of the capacity/potential difference curves obtained at —38 C, with and without addition of nonanol, coincided owing to the total desorption of nonanol from the homogeneous surface of liquid mercury. At —41 C, the curves did not coincide, confirming the view that total desorption does not take place in the case of a solid (heterogeneous) metal electrode [cf. *ibid.*, No. 1, 101-104 (1954)]. The hydrogen overvoltage changed at —41 C in the presence of nonanol by ~400 mV, a value close to the adsorption potential measured by the displacement of the minimum of capacity in dilute solution of sulfuric acid.—MA.   9111

3.6.8, 5.8.3, 4.7
Influence of Surface-Active Agents on the Overpotential of Hydrogen on Platinum. (In Russian). V. L. KHEIFETS AND B. S. KRASIKOV. *Doklady Akad. Nauk SSSR*, **94**, No. 1, 101-104 (1954).

The minima of capacity of the electrolytic double layer were measured in 2N-sulfuric acid, 0.5N-sodium sulfate, and 0.5N-sodium hydroxide solutions with addition of caprylic acid, sodium caprylate and diphenylamine. The changes of the hydrogen overpotential on a smooth platinum electrode calculated from these measurements agree with the values of adsorption potentials of the same surface-active agents determined in 0.02-N solutions of the three electrolytes. Diphenylamine behaved as a cation in sulfuric acid solution, increasing the hydrogen overpotential; sodium caprylate as an anion in sodium sulfate solution, decreasing the overpotential. The desorption of the surface-active agents during an appreciable displacement of the electrode potential in either the positive or negative direction was not complete on platinum, in contrast to the phenomena observed on mercury [cf. Proskurnin and Frumkin, *Trans. Faraday Soc.*, **31**, 110 (1935)]. This fact was attributed to the heterogeneity of the platinum surface as compared with that of liquid mercury.—MA.   9113

3.7 Metallurgical Effects

3.7.2, 3.2.2, 3.5.9
The Effect of Composition on the Scaling of Iron-Chromium-Nickel Alloys Subjected to Cyclic Temperature Conditions. H. L. EISELSTEIN AND E. N. SKINNER. Paper before Am. Soc. Testing Materials Symp. on Effect of Cyclic Heating and Stressing on Metals at Elevated Temperatures, 57th Ann. Mtg., Chicago, June 17, 1954. ASTM Special Technical Pubn. No. 165, 1954, 162-172; disc., 172.

Scaling behavior of a number of iron-chromium-nickel alloys was examined under cyclic conditions involving 15 min.

heating in air, followed by 5 minutes air cooling. "A" Ni, 80-20, Nimonic 75, Inconel, 60-15, Incoloy, 6 stainless steels, and a number of experimental alloys specially prepared from laboratory melts were tested. Results for test temperatures of 1400, 1600 and 1800 F permit mapping of alloy compositions in terms of ability to resist scaling or flaking of oxide films. While nearly all compositions are satisfactory at 1400 and 1600 F, scaling is pronounced at 1800 F for alloys containing less than 35 percent nickel and less than about 20 percent chromium at low end of nickel range and less than about 15 percent chromium at high end of range. Tables, graphs.—INCO.   9259

3.7.3
Dry Hydrogen Brazing for High Strength Alloys. F. C. KELLEY. *Product Eng.*, **25**, No. 8. 156-160 (1954) August; *Machinist*, **98**, No. 41, 1786-1790 (1954) October 8.

Parts are heated with brazing metal in pure dry hydrogen. Brazing alloys mentioned include the hard surfacing alloy containing 65-75 percent nickel, 13-20 percent chromium, 2.75-4.75 percent boron, 10 percent maximum (iron, silicon, carbon). Basis metals brazed are stainless steels, Nichromes, Stellites, low-expansion alloys (nickel-iron, iron-nickel-cobalt) and others; metal/ceramic joints can be made after coating the ceramic with TiH. Gives design and joint strength data.— BNF.   9198

3.7.3
Welding Methods Used in the Construction of Oil Refineries in General and of The Shell Oil Refinery at Geelong in Particular. P. Josso. Paper before Australian Welding Convention, Melbourne, October 5, 1954. *Australasian Engr.*, **1954**, 46-53, Dec. 7.

Welding of vessels for the oil industry, welding of pipelines, including heat-resisting pipelines, stud welding, application of alloy steel linings for corrosion protection and welding of petroleum storage tanks are considered. Good results are obtained in welding of chromium-molybdenum heat-resisting steel pipes with use of high-alloy welding rods of a 25% chromium- 20% nickel, 18% chromium— 8% nickel —3% molybdenum, or 18/12/3 types. Welding of lining materials with high expansion coefficients, such as 18% chromium—10% nickel steels and 17% chromium-12% nickel—3% molybdenum steel, is described. When a lining consisting of strips of 12% chromium steel is welded to a carbon steel vessel wall with only two welding beads, 25% chromium-20% nickel electrodes should be used to obtain a weld that is sufficiently corrosion-resistant. When three welding beads are applied, electrodes depositing a lower alloy content, such as 19% chromium-9% nickel-3% molybdenum, may be used. Diagrams.—INCO.   9197

3.7.3
Effect of Heat Treatment on Fatigue Strength of Steel During Atmospheric Corrosion. (In Russian). A. V. RIABCHENKOV AND E. L. KAZIMIROVSKAIA. *Vestnik Mashinostroeniia*, **35**, No. 1, 69-72 (1955) Jan.

Case-hardening; normalizing; mircostructures. Graphs, table, micrographs. 6 references.—BTR.   9220

3.7.3, 1.6, 6.4.2
Ultrasonic Soldering of Aluminum. J. BYRON JONES AND JOHN G. THOMAS. Aeroprojects, Inc. for E. I. du Pont de Nemours

and Co., Exposives Dept. Atomic Energy Div. (Contract AT(07-2)-1, Dec., 1954, 81 pp.

Aluminum joints including one zinc-aluminum-silicon and nine tin-zinc-aluminum solder compositions were appraised for resistance to corrosion in an environment of 95 C, aerated, distilled water. The effect of pure zinc and pure aluminum metal oversprays on extending the life of soldered aluminum joints was examined, with the aluminum spray proving to be effective. A soldered joint life up to about 1000 hours in the stipulated environment is indicated. Avenues for potential improvement in corrosion resistance of soldered aluminum joints are suggested. (auth).—NSA.   9127

3.7.3, 3.6.6
Resistance Welding Joins Dissimilar Metals. *Industry & Welding*, **27**, No. 9, 65-67, 113 (1954) October.

Summary of spot welding condition for combinations of dissimilar metals, including nickel to mild steel, nickel steel, 18-8, Monel and Inconel; Monel to mild steel, nickel steel, 18-8 and Inconel; Inconel to mild steel, nickel steel and 18-8; and 18-8 to mild steel and nickel steel is tabulated. —INCO.   9150

5. PREVENTIVE MEASURES

5.3 Metallic Coatings

5.3.1, 5.4.1, 5.9.1, 1.6
Protective Coatings for Metals. R. M. BURNS AND W. W. BRADLEY. Book, Second Edition, 1955, 643 pp. Reinhold Publishing Corp., 430 Park Ave., New York 22, New York.

This book, which has been thoroughly revised to include developments in coatings during the fifteen years since publication of the first edition, is intended principally for the person who uses coatings to protect metals. Information relative to formulation is included, where needed, to clarify applicatory problems. In both foreword and preface substantial notice is taken of the urgent need to preserve metal resources by limiting corrosion.

The first chapter is devoted to principles of corrosion and corrosion control, describing how metals react with their environment and how these reactions may be controlled. Comprehensive discussions on surface preparation, types of metallic coatings, sprayed metal coatings, production and properties of zinc coatings, and cadmium coatings and their protective value follow.

Additional chapters follow on coatings of copper, lead and other metals and alloys, noble metals, methods of testing, organic coatings, application and use of organic coatings, chemical conversion and anodized coatings, special purpose coatings and corrosion inhibitors.   8771

5.3.1, 5.9.1, 1.6, 2.3.7, 2.4.3
Yearbook of Surface Technology. (In German). W. WIEDERHOLT, Editor. Book, 1954, 704 pp. Metall-Verlag G.m.b.H., 18 Hubertusallee, Berlin-Grunewald.

Does note attempt to be complete manual of metal finishing although the whole field is covered briefly, with stress on recent advances in the technique of metal finishing and of testing of deposits. General survey (30 pp.); metallizing of nonconductors with liquid preparations (2 pp.); new German patents (20 pp.); methods and apparatus for assessment of sufraces

(30 pp.); conditions of deposition of common metals (25 pp.); alloy deposits (25 pp.); Hull cell tests (15 pp.); non-destructive thickness testing (15 pp.); spectrographic analysis in electrodeposition (40 pp.); index to world literature 1950-53 (60 pp.).—BNF.   8919

5.3.2
Electroplated Applications for Precious Metals. I. CROSS AND P. J. SLOANE. Harper-Leader, Inc. *Elec. Mfg.*, **55**, No. 1, 96-99 (1955) Jan.

Properties and applications of electrodeposits of the precious metals, silver, gold, platinum, rhodium and palladium, are summarized. Group as a whole is characterized by high resistance to surface changes which makes it valuable for electrical and electronic applications. Where wear resistance and constant surface properties are important, rhodium is the preferred metal and can be applied from 0.000005-0.001 in. Gold, palladium, and rhodium in thin deposits are used over heavier plates of silver where preservation of the high conductivity of the underlying silver is important. Platinum is used in special applications involving high temperatures or extremely corrosive conditions. Tables and 6 references.— INCO.   8788

5.3.2, 2.3.7
Test Gives Bond Life Expectancy of Bimetallic Materials. J. B. MOHLER. *Iron Age*, **174**, No. 10, 106-107 (1954) Sept. 2.

Experiments on bond deterioration and expected service life of aluminum-clad steel sleeve bearings. Bond strengths were determined by the shear test on specimens heated to various temperatures.— BNF.   8876

5.3.2, 5.4.1, 3.5.9
Protective Coatings on Metals Against Scaling at High Temperatures. (In German). O. VON GOLDBECK. *Metalloberflache*, Series A, **8**, No. 6, A81-A85 (1954) June.

A general survey based on 31 references and covering all types of coatings: metallic, non-metallic, ceramic, etc.— BNF.   8832

5.3.4
Flashes on Galvanized Sheet. (In German). H. J. WIESTER AND D. HORSTMANN. *Stahl und Eisen*, **74**, No. 13, 835-838 (1954).

Study of this defect (areas of roughness), which may be due to scale, etc., deposited on the steel surface, or to hydrogen adsorbed during pickling, which has collected at elongated silicate inclusions.—BNF.   8768

5.3.4
Effect of Rapid Cathode Rotation and Magnetic Fields on Crystal Orientation in Electrodeposited Metals. L. YANG. *J. Electrochem. Soc.*, **101**, No. 9, 456-460 (1954) September.

Metals deposited were nickel, iron, silver, copper and antimony. Rotation at 3,000 r.p.m. had various effects on orientation; a magnetic field perpendicular to the cathode produced very rough deposits.—BNF.   8770

5.3.4
Barrel Plating Electrolytes, E. E. HALLS. *Product Finishing*, **7**, No. 4, 72-82 (1954) April.

The author points out that many variables are associated with barrel plating and that success can only be achieved gradually. This article is concerned chiefly with electrolytes, and practical data based upon satisfactory results obtained in

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practice are presented. Zinc, nickel, cadmium, tin, copper, silver and gold electrolytes are discussed, typical electrolyte compositions and the results obtained under suitable operating conditions being described.—ZDA. 8875

5.3.4
"Curtain Formation" on Galvanized Sheet and Hollow-Ware. (In German). H. J. WIESTER AND D. HORSTMANN. *Stahl und Eisen,* **74,** No. 13, 831-834 (1954).
Discusses fringe-like tear formation

along areas of uneven flow; metallographic investigation led authors to attribute it to the presence of fine iron particles remaining on the surface after steel with adherent scale had been annealed in a strongly reducing atmosphere.—BNF. 8834

5.3.4, 1.3, 3.7.3
The Influence of the Physical Metallurgy and Mechanical Processing of the Basic Metal on Electroplating. Pt. I. Critical Review of Electroplating. A. E. R. WESTMAN AND F. A. MOHRNHEIM. American Electroplaters Res. Project No. 14; *Plating,* **42,** No. 2, 154-158, 195 (1955) Feb.
Literature survey summarizes previous work on influence of physical metallurgy and mechanical processing of basis metal on electroplating. Investigation is limited to the study of steel as a basis metal for the deposition of nickel and nickel-chromium coatings. Study indicates that there is need for a more metallurgical approach to the problem and for more closely controlled experimentation in this field, starting with the effects of the microgeometry of basis metal. Comprehensive biblio on influence of basis metal in electroplating is presented.—INCO. 8907

5.3.4, 6.2.2
Chromizing of Spheroidal Graphite Cast Iron. S. UEDA. *Repts. Casting Res. Lab., Waseda Univ.,* No. 5, 39-41 (1954).
It is evident that spheroidal graphite cast iron can be chromized by means of chromium chloride process. A layer, rich in chromium, was obtained under the treatment conditions such as 1,000 C, 5 hour period and 50 cc./min. gas velocity. Wear test in dry state conducted on nitrided drum showed that chromized spheroidal graphite cast iron gave wearloss half as much as that of untreated spheroidal graphite cast iron and 2/3 as much as that of same hard-chromium electroplated. Photomicrograph, graph and two references.—INCO. 8813

5.3.4, 8.8.5
Temperature Control Key to Longer Pot Life. W. G. IMHOFF. Wallace G. Imhoff Co. *Iron Age,* **175,** No. 3, 92-94 (1955) Jan. 13.
Investigation of mechanics of zinc-iron alloy formation in hot-dip galvanizing. Small square of 28 gage one-pass cold-

rolled sheet iron was used in study of contact of iron with molten zinc at 800-1000 F (every 50 degrees), and at 1100, 1300 and 1500 F. Iron contents of melts (obtained in clay crucibles), which varied with dissolving action of galvanizing zinc on base metal, are tabulated, and photomicrographs show grain structures at test temperatures. Dissolving actions and recrystallizations which take place are described. Photomicrographs of zinc-iron alloy crystals are shown. For long equipment life, galvanizing bath temperatures under 885 F and uniform application of heat are recommended. Above 900 F dissolving action becomes increasingly violent, and at 1100 F or above, pot will eventually fail with a hole dissolved through side. Graph.—INCO. 8785

5.4 Non-Metallic Coatings and Paints

5.4.1, 5.3.1, 5.9.1, 1.6
1955 Finishing Handbook and Directory. Book, 1955, 484 pp. Sawell Publications Ltd., 4 Ludgate Circus, London E.C. 4.
Fifth edition. Book. extends information on finishing materials to 294 pages to include sections on chief types of paint, selection of paint schemes, paint application methods, finishes for aluminum alloys. Other subjects include anodizing, applied plastic coatings, electroplating, flock coating, preparatory treatments and vitreous enamelling. Glossary of finishing terms and list of conversion factors and solvent flash points are provided.
Directory of equipment, plant and materials used in finishing field, out-working firms, and trade and brand names is revised and extended to 192 pages. For easier reference, section on finishing equipment is divided into general classifications corresponding to sections in handbook such as preparatory treatments, paint applications of equipment and plant and supplies for electrolytic processes. Included with each out-working firm's entry is information as to other finishing processes carried out and classification of these into geographical areas based on main British industrial centers. 8765

5.4.2
Use of Cast Iron Ground-Coats. P. ROGERS. Paper before Inst. of Vitreous Enamellers Summer School. *Foundry Trade J.,* **98,** No. 2005, 121-123 (1955) Feb. 3.
Ground-coats used when enamelling cast iron are grouped into three main types: vitreous or glossy, annealing-type, and matte ground-coat. They are discussed separately, describing their application, advantages, disadvantages and methods to be used if they are to achieve the desired object of controlling re-boil.—INCO. 8752

5.4.5
Ths Use of Silicone Resins in Protective Coatings. T. W. WATSON. *Bull. Inst. Metal Finishing,* **4,** No. 4, 299-306 (1954-1955) Winter.
100% silicone resins are used in specialized applications where organic media are unsuitable. Use is made of high temperature and oxidation stability, together with comparative inertness and resistance to chemical and corrosive attack. Applications for silicone resin containing paints are to be found where superior heat or weathering resistance is desired. Thus they are used on hot metal surfaces such as furnace stacks, heating ducts and

heaters. High temperature properties of these resins plus their low moisture absorption has led to their adoption as insulating materials.—INCO.   8835

5.4.5

Sealing Metal Surfaces with Resins (Araldite). A. E. WILLIAMS. *Ind. Finishing*, **6**, No. 70, 635-641 (1954) April.

Physical and chemical properties of ethoxylene resins ("Araldite"), in particular strong adhesion to metals (especially aluminum and magnesium); hardness and flexibility; corrosion resistance; method of application; uses as coatings for ferrous and non-ferrous metals and as a base coat for painting.—BNF.   8828

5.4.5

Asphalt Emulsions as Protective Coatings. C. C. WEEKS. Paper before Chem.

Inst. of Can., Protective Coatings Div., Toronto, June 21-23, 1954. *Chem. Can.*, **6**, No. 10, 33-37 (1954) Oct.

Properties of asphalt which make it important as a coating material include good resistance to transmission of water and water vapor, good chemical resistance to acid and alkaline solutions, availability and economy. Industrial asphalt solutions, possessing all of the properties of solid and semi-solid asphalts, are even more advantageous as coatings since they overcome the problem of cold flow, eliminate almost completely the tendency to crack and alligator under weather exposure, and are easier to apply.—INCO.   8821

5.4.5

Vinyl Emulsion Coatings in Theory

and Practice. Part II. O. H. ULRICH. *Paint Technol.*, **18**, 9-12 (1954) September.

Practical aspects of manufacture, characteristics, and application. 1 reference.—BTR.   8804

6.   MATERIALS OF CONSTRUCTION

6.6   Non-Metallic Materials

6.6.8, 8.4.3, 1.7.1

Reports to Technical Unit Committee T-1J on Oilfield Structural Plastics. Part 2. Structural Behavior of Unplasticized Geon Polyvinyl Chloride. G. F. MALONE. Nat'l. Assoc. Corrosion Engrs. Pubn. No. 55-7; *Corrosion*, **11**, No. 6, 283t-287t (1955) June.

Reports of an investigation of the effects of temperature on the physical properties of Geon non-plasticized polyvinyl chloride and the effect of temperature on short term tensile properties are given. The tests show that at relatively low stresses the deflection and rate of creep are directly proportional to applied stress. Above some stress limit varying between 2200 and 3000 psi deflection and rate of creep increase very much faster than stress. A minimum safety factor of 5 to 1 or 20 percent of ultimate tensile strength should be used.   9108

6.6.8, 8.4.3, 7.2, 1.7.1

Reports to Technical Unit Committee T-1J on Oilfield Structural Plastics. Part 1. Long-Term Creep of Pipe Extruded from Tenite Butyrate Plastic. L. W. A. MEYER AND R. J. SCOGIN. Nat'l. Assoc. Corrosion Engrs., Pubn. No. 55-7; *Corrosion*, **11**, No. 6, 277t-283t (1955) June.

Data are given of creep of extruded Tenite Butyrate pipe under internal pressure. Nine-foot lengths of pipe were maintained under different internal pressures. Data are given in 16 graphs showing individual creep data and four graphs summarizing each of four groups. Tables are given showing safe hoop stress values with corresponding tensile strength data.   9107

6.6.8, 8.8.1

Glass Fibre Reinforced Plastics in the Chemical Industry. F. F. JARAY. *Engineer*, **193**, 839-842 (1954) December 7.
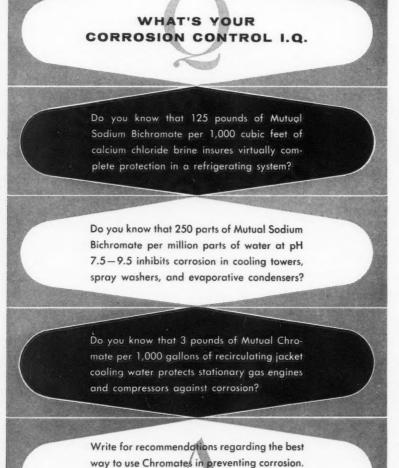
Details of materials, with notes on some successful applications. Quantitative corrosion data are given and strength of laminated plastics discussed.—INCO.   9128

6.6.5

Carbon and Graphite as Resistant Materials. Part II. M. BUIS. *Corrosion Prevention and Control*, **2**, 37-40, 58 (1955) Feb.

Fabrication and use in plant construction. Table, graph, photograph. (To be continued.)—BTR.   9232

6.6.6

Effects of Some Metal Additions on Properties of Molybdenum Disilicide. H. A. DEVINCENTIS AND W. E. RUSSELL. U. S. Nat'l. Advisory Comm. Aeronaut., Research Memo., E54B15, 1954, 22 pp.

Powdered molybdenum disilicide, mixed with 6% nickel, cobalt, or platinum, was hot-pressed at 2800 F (1540 C) under 2500 lb./in.₂ The sintered samples were homogenized in helium as follows: cobalt bearing, at 2000-2400 F (1095-1315 C), nickel bearing at 1800-2400 F (980-1315 C), and platinum bearing at 2400-2600 F (1315-1425 C). The principal results are:

a) Nickel bearing: Modulus of rupture is about ⅓ that of pure molybdenum-disilicide. No uncombined nickel is present after hot pressing. Low-melting point intermetallic compounds are formed above 2000 F. Oxidation resistance is decreased and thermal-shock resistance is unchanged by nickel addition. b) Cobalt-bearing: No uncombined cobalt is present after hot pressing. Mechanical properties are better than for nickel-bearing alloys. Oxidation-resistance is less than for pure molybdenum disilicide and thermal-shock resistance is unchanged. Low-melting point intermetallic compounds are formed above 2200 F (1200 C). c) Platinum-bearing: Strength is much lower than for molybdenum disilicide. Oxidation-resistance up to 2000 F is comparable to that of molybdenum disilicide, but lower at higher temperatures. Uncombined platinum is present in high-pressed samples, but disappears after heat-treatment at the higher temperature. Thermal-shock resistance is unchanged.—MA.   9265

6.6.6
Contribution to the Zirconium-Silicon System and Some Mixed Silicide Systems. (In German). R. KIEFFER, F. BENESOVSKY AND R. MACHENSCHALK. *Z. Metallkunde,* **45,** No. 8, 493-498 (1954) August.

Literature review and original work on zirconium-silicon system (sintered specimens, 0-90% silicon); crystal structures, mutual solubility and scaling resistance of ZrSi₂-TiSi₂ and ZrSi₂-VSi₂.—BNF.   9273

6.6.8, 1.7.1, 8.4.3, 7.5.5, 7.2
Summary of Data on Use of Structural Plastic Products in Oil Production. A Status Report of NACE Technical Committee T-1J on Oilfield Structural Plastics Including Appendices 1-4. W. M. THORNTON, Chairman AND B. W. BRADLEY, Vice-Chairman. *Corrosion,* **11,** No. 6, 59-69 (1955) June.

The report covers results of a questionnaire survey to determine experience to date. The most quantitative data developed by the survey were the strapping data on a 250-barrel glass-polyester and a like-size glass-epoxy tank. After two years the glass-polyester tank was still creeping and subject to 0.152% volume change due to temperature difference between winter and summer. Not enough data are available on the glass-epoxy tank to determine creep rate, but it was noted that the volume change between winter and summer was about 0.10%.

Appendix I. Service Experience of 11 Oil Field Installations of Glass Reinforced Plastic Tanks: Data cover two types of laminates in both constant load and fatigue type tests. Although the tests were not complete at the time the data again indicated the large difference in short-term strengths in air and the long-term strengths in the service environment. In this case fatigue strengths seemed higher than stress rupture strengths thereby indicating repeated tank fillings might not be a more severe service than a tank continually full.

Appendix II. Service Experience of 28 Oil Field Installations of Glass Reinforced Plastic Pipe: This report presents data obtained by questionnaire survey. The data on centrifugally cast pipe show that failures have occurred in 57% of the 21 reported installations. The data further indicate that the service of these materials is adversely affected by temperatures above atmospheric and pressures above 100 psi.

Appendix III. Oil Field Structural

Plastic: This report presents data obtained by questionnaire survey. The few reported installations do not allow general conclusions to be drawn concerning the economic value of plastic tubing. At the time of the questionnaire survey, five installations were serving without history of failure. These five installations were between 3003 and 3860 ft. in length. Two had served 16 months, one 12 months, one 9 months and one 6 months. All were centrifugally cast glass reinforced tubing used as induction strings in salt water disposal wells.

Appendix IV. Laboratory Tests on Reinforced Plastic Tank Materials: Data are tabulated for plate fatigue and stress rupture tests.   9203

6.6.8, 7.2, 8.9.3
Plastic Pipe for Underground Structures. RAYMOND B. SEYMOUR. *Corrosion,* **11,** No. 7, 322t-327t (1955) July.

Tabulated data are given on the physical properties of pipe made from the epoxy-glass, polyester-glass, cellulose acetate butyrate, polyethylene, styrene-rubber, polyvinyl chloride, Type I and polyvinyl chloride, Type II as to specific gravity, tensile strength, flexural strength, thermal expansion, impact and maximum useful temperature together with extensive information on their chemical resistance versus natural and artificial gas, salts, caustics, petroleum crude and hydrochloric acid. Impact and temperature characteristics also are reported.

Tabulated information also includes statistics on the relative volume of the subject plastics in use as well as the specifications for several kinds of plastic pipe.
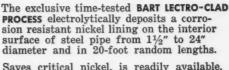
The author proposes specifications for an ideal pipeline and covers in narrative and in mathematical equations some of the essential engineering characteristics of correctly used plastic pipes.   9121
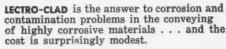
7. EQUIPMENT

7.1 Engines, Bearings and Turbines

7.1
A White-Metalling Process for Bearings. Monometer Manufacturing Co., Ltd. Ind. *Gas* (England), **17**, No. 200, 256, 258, 260 (1954) May.

Lining axle-box bearings for railway rolling stock with 56 tin—30 lead—11 antimony—3% copper whitemetal by pressure die casting. Bearing shell is of cast copper—7 tin—5 zinc—2 lead—1% maximum nickel and is previously machined, stopped-off with French-chalk and isinglass and tinned by hot-dipping.—BNF. 　　　　9179

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7.2 Valves, Pipes and Meters

7.2, 6.6.11
Advantages of Wood Lined Steel Pipe in Corrosive Services. E. H. BRONSTEIN. *Corrosion*, **11**, No. 5, 205t-209t (1955) May.

Wood-stave and especially wood-lined steel pipe is extensively used to transport corrosive and abrasive substances at temperatures up to 185 F. Wood is especially useful in handling pulp suspensions, pulp-mill wastes, mine wastes, dilute mineral acids and dilute caustic soda solutions. Its acceptable pH range is from 2.5 to 11. It is not recommended for use with strong oxidizing agents, concentrated mineral acids or highly alkaline or caustic solutions. It is used successfully to exhaust many kinds of corrosive fumes and vapors.

Short term laboratory and lengthy service experience have shown that even under pressures up to 100-200 psi liquids seldom penetrate halfway through standard thicknesses of staves. This keeps corrosion at the wood-steel interface of wood-lined pipe at a minimum.

Other assets are sustained low friction coefficients and a degree of insulation from temperature. 4 tables, 16 references and bibliography. 　　　　9125

7.3 Pumps, Compressors, Propellers and Impellers

7.3
Pumps. T. HICKS. *Power,* **98**, No. 10, 75-106 (1954) October.

Pumping principles, applications and selection of centrifugal, rotary and reciprocating pumps are discussed. A table lists materials (including nickel and nickel alloys, Monel, 18-8) to be used in the principal parts of centrifugal pumps. Materials are chosen for their ability to resist the corrosive attack of the liquid being pumped. Many illustrations and graphs.—INCO. 　　　　9184

7.4 Heat Exchangers

7.4.2, 4.2.3, 2.4.2
Corrosion Studies on a Model Rotary Air-Preheater. G. G. THURLOW. *Proc. Inst. Mech. Engrs.*, **168**, No. 20, 571-578 (1954); *Corrosion*, **11**, No. 6, 267t-274t (1955) June.

Tests have been carried out on a model rotary air heater in an attempt to study, on a laboratory scale, corrosion phenomena under conditions similar to those experienced in industrial practice.

The acid dew-point of the combustion gases used varied from 240 to 320 F and maximum corrosion occurred at surface temperatures within the range 215-240 F. The results confirm previous conclusions as to the influence of the acid dew-point and of the sulfur trioxide content of the gases on corrosion. 　　　　9122

7.4.2, 4.6.4, 3.5.11
Material Selection for Condenser Tubes. HAROLD A. TODHUNTER. *Corrosion*, **11**, No. 5, 221t-226- (1955) May.

Factors involved in the design and operation of sea water condensers are discussed. These include water conditions and design factors which may affect condenser tubes life. Effect of water velocity is surveyed and a study is given of relative costs of cooling water systems for different velocities. Specific cases are cited involving Los Angeles Harbor water including methods considered and used to regulate animal and plant life. Effects of chemicals, galvanic action and design of tubes of various alloys are explored. Economic data involved are cost of fuel, generating capacity, expectant life of plant and other criteria. An appendix gives a brief history of 1500 tubes installed in a sea water condenser in August 1947. 　　　　9193

7.4.2, 6.4.2
Aluminum Alloy Oil-Tanker Heating Coils. *Engineer*, **198**, No. 5137, 62 (1954); *Engineering*, **178**, No. 4614, 28 (1954).

A system of aluminum alloy heating coils has been developed to replace the mild-steel or cast-iron coils usually employed. The coils carry steam and are used to raise the temperature and hence

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lower the viscosity, of the crude oil in the tanker cargo compartments, so that pumping operations are facilitated. The aluminum coils in heating efficiency, are equal to mild-steel coils in heating efficiency, are free from corrosion and result in a considerable saving in weight in the heater installation. —MA.   9269

7.10 Other

7.10, 3.5.8
Method of Preventing Fatigue Failure of Steel Bolts. R. H. CROSS AND G. M. NORRIS. *Engineer,* **198,** 410-411 (1954) Sept. 24.

Use of two nuts locked together can prevent fatigue of a bolt in tension.— BNF.   9258

7.10, 6.2.1, 6.3.6, 6.3.10
Corrosion Control in Coil-Spring Manufacture. CHARLES HARRIS. *Corrosion Technology,* **1,** No. 10, 376-379 (1954).

As well as ferrous materials, brief reference is made to brass, phosphorus bronze, copper-beryllium and nickel alloys for spring manufacture. Various methods of protecting steel springs may be used, including electro-deposition of nickel, zinc, or cadmium.—MA.   9132

7.10, 6.2.5
Stainless Springs Have Long Service Life. *Iron Age,* **173,** No. 14, 149 (1954) April 8.

Type 301 stainless is giving superior service life in installations requiring constant flexing at high speeds over long periods of use. Stainless steel springs (1 ribbon coil and 2 flat diaphragm springs) are used in Addressograph-Multigraph

Corp.'s Class 1900 machine because of their superior physical properties rather than corrosion resistance. Illustration.— INCO.   9202

7.10
Fireproof Dock Serves Refinery. *Eng. News-Record,* **153,** No. 17, 34-37 (1954) October 21.

Steel H-piles with Gunited coatings are used in construction of fire-proof oil loading wharf. Steel section provides resistance to bending during driving. 2-inch thick Gunite coating, reinforced by wire mesh, protects piles against salt water corrosion.—INCO.   9274

8. INDUSTRIES

8.2 Group 2

8.2.2
Special Corrosion Problems of Electric Utility Systems. C. F. AVILA AND A. B. JONES. *Corrosion,* **11,** No. 7, 291t-294t (1955) July.

Details concerning the cause of several cases of corrosion of outside plant of electric power companies and remedies adopted for mitigation are given. Included are discussions of corrosion problems involving corrosion cracking, galvanic action, ground line corrosion of standpipes, water pockets, horizontal surfaces, joints, concrete corrosion of lead, nitrous oxide attack where corona forms. Specifications and details for construction and protection of a zinc sprayed subway transformer tank are given.   9194

8.4 Group 4

8.4.5, 4.7
Heat Exchange in Liquid Metal Fuel Power Reactor Systems. O. E. DWYER. Brookhaven Nat'l. Lab. *Nucleonics,* **12,** No. 7, 30-39 (1954) July.

Underlying principles and factors affecting design of heat transfer components in liquid metal fuel reactors are discussed and calculations for typical system designs are presented. Graphite is used inside the core and Croloy 5-Si, outside. Their lack of nickel makes Croloy ferritic steels better than regular stainless steels for minimizing the problem of mass transfer by bismuth, but they have less oxidation resistance at elevated temperatures and generally poorer physical properties than regular stainless steels. Croloy 5-Si tubes in the externally cooled reactor described are ⅛ inch thick to insure against tubes falling apart from corrosion and spacing between tubes is ¼ inch for all tube sizes to prevent plugging by buildup of intermetallic solids. Tables, 7 references.—INCO.   9257

8.8 Group 8

8.8.1
Manufacture and Use of Chlorine Dioxide at Riegel Carolina. J. D. DAILEY. Riegel Carolina Corp. Paper before Am. Pulp & Paper Mill Supts. Assoc., So. & Southeast Div., Asheville, N. C., October 13-15, 1954. *Paper Trade J.,* **138,** No. 51, 34, 36, 38 (1954) December 17.

Description of the original chlorine dioxide manufacturing plant and changes to the original equipment, including new reactors. The circulation rotometer floats in the original plant, although made of Hastelloy C or Durimet 20, did not stand up. Corrosion and erosion caused the floats to become unbalanced. Reactors made of steel with an acid-proof brick lining backed up by an Atlastavon 20 membrane were installed in present plant and circulation is measured and recorded by an orifice meter for each reactor. In the original chlorine dioxide bleaching plant, the mixer was a vertical double shaft mixer with mild steel rotating elements covered with Hastelloy C., and acid-brick-lined steel shell. The Hastelloy failed by corrosion and erosion after about one year and a single shaft Hastelloy C mixer was installed as a replacement. Illustrations.—INCO.   9263

8.8.3, 8.8.5
Protection of the (Internal) Surfaces of Plating and Ancillary (e.g. Pickling) Equipment. A. FOULON. *Metalloberflache,* Sec. B, **6,** No. 3, 42 (1954).

A note on constructional and lining materials suitable for plant subjected to the corrosive solutions employed in plating and ancillary operations.—MA. 9250

8.8.5, 4.7, 6.2.2, 5.3.4
The Attack of Iron-Saturated Molten Zinc on Silicon-Containing Iron. (In German). D. HORSTMANN. *Arch. Eisenhuttenw.,* **25,** No. 11/12, 527-533 (1954) Nov.-Dec.

Report of basic investigation which leads to the conclusion that silicon content of irons for galvanizing kettles must be held as low as possible. Experiments were made on irons containing up to 4.86 % silicon. Effects of temperature (430-550 C) and time and structures and growth of iron-zinc alloy protective layers are discussed.—INCO.   9180

8.9 Group 9

8.9.3
How to Combat Internal Corrosion. RUSSELL A. BRANNON. *Pipe Line Industry,* **2,** 44-49 (1955) March.

Corrosion protection by means of coatings and inhibitors. Photographs, diagrams, table.—BTR.   9230

8.9.3, 5.4.5
Coating Pipelines in Place Internally with Plastics. J. C. WATTS. *Corrosion,* **11,** No. 5, 210t-216t (1955) May.

Since 1947 various materials including baked phenolics, air drying vinyls, thermosetting polyesters, furanes and others have been used with varying success for the internal coating in place of pipe lines. Development of high-solids vinyls and amine cured epoxies has made the process more dependable.

Principal problem in applying the coatings is in surface preparation. The author recommends a scheme involving successive cleaning by abrasion, solvent cleaning, alkaline cleaning and acid cleaning with the necessary intermediate washings. Drying is effected best by aspiration until the coating is thoroughly dry. "Solvent washing" resulting from the condensation of solvent at cool places in the pipe is a primary difficulty in the drying process. Tests of drying times are reported.

Considerable data on economics of internal coating on about 100,000 ft. of pipe are given, indicating payout for some types of service in short lines in as short a time as on year. Economics of internal

plastic coating are not as good for long lines as for short ones. Several case histories of lining economics are given.

Collateral benefits in improved flow capacity and reduction of paraffin deposits are reported.

Factors to be considered when planning an internal coating job are given.   9208

8.9.3, 5.8.2, 2.3.4

Control of Internal Corrosion of a Product Pipe Line System. P. L. DE-VERTER AND A. W. JASEK. *Corrosion*, 11, No. 6, 261t–266t (1955) June.

This article considers the matter of controlling internal corrosion in a products pipe line system and reports experience with two control methods. A laboratory method of evaluating a particular oil soluble inhibitor is described, as well as the application of the laboratory method to control the degree of protection in the pipe line and to facilities beyond the pipe line. A specific method of determining the amount of inhibitor in the product also is discussed and proper interpretation of the laboratory data is emphasized.

Experience referred to covers the corrosion control in a single 8-inch products pipe line transporting only premium and regular grades of motor fuel and 100 and 115 grades of aviation gasoline. This includes use of a water soluble inhibitor for several years but because the degree of protection desired was not realized and because the protection ended at the pipe line terminus, decision was made to substitute an oil soluble inhibitor. Factors considered in selecting the oil soluble inhibitor included cost, effect on product specifications and the degree of protection desired both in the pipe line and to equipment beyond the pipe line.

Results indicate that benefits realized through the use of an oil soluble inhibitor more than offset its higher cost compared to the water soluble type. The article mentions briefly the attitude of the U. S. Air Force Materiel Command, which indicates the direction of general acceptance of the use of oil soluble inhibitors, at least in systems handling fuels for the U. S. Air Force.   9204

8.9.3, 7.5.5, 8.4.3, 1.2.2

Economic Considerations in Pipe Line Corrosion Control. L. G. SHARPE. *Corrosion*, 11, No. 5, 227t–240t (1955) May.

Three major corrosion problems encountered in pipe line operation are considered. Experience with the various corrosion control methods is described and the economics of their use is examined.

Internal Corrosion in Sour Crude Oil Pipe Lines—For controlling internal corrosion in sour crude oil pipe lines, corrosion inhibitors, regular scraper runs, internal coatings, concrete lining, asbestos-cement pipe and plastic pipe all are effective and economical.

External Corrosion of Oil Storage Tank Bottoms—Slightly more than 5% of the unprotected oil storage tank bottoms in a large pipe line system fail each year as a result of soil corrosion. Cathodic protection effectively controls corrosion at an average installation cost of $410 per tank and an average total operating expense of $62 per tank per year.

This installation cost is equivalent to about 3% of tank bottom investment; the total annual operating expense is equivalent to about 1¼% of one repair job. Protection of all remaining unprotected tank bottoms in the system would have an indicated payout of 1½ years; the total annual operating expense of such protection would amount to about 25% of the present annual direct cost of tank bottom repair.

External Pipe Coatings and Cathodic Protection—Substantial coatings supplemented with cathodic protection are used generally for preventing external corrosion of buried pipe lines. Relationship between coating practices and costs and cathodic protection requirements and costs is examined and conclusions are given.   9207

8.9.5

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Report on types and causes of corrosion on ships and evaluation of preventive methods. Photographs, tables, graphs, diagrams. 26 references.—BTR.   9244

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Consumption of anodes in the process; form of erosion; suitability of different types of coke and binding agents; fabrication of anodes.—BNF.   9130

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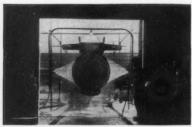
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KEL-F® dispersion-coated tank truck transports corrosive chemicals

BAKE OVEN at Kellogg Plant, Jersey City, N.J. Overall length 85 ft., width 12 ft., height 12 ft., iso-thermal control, ±5°F. This new Kellogg oven is being used to develop improved techniques for large area applications.

QUENCHING—After final baking, tank is quenched to produce tough, transparent, flexible coating.

This tank, which is designed to transport corrosive chemicals without danger of contamination of the final product, was spray coated with KEL-F Dispersions at the Kellogg plant in Jersey City, and baked-fused in a specially built oven large enough to complete each coating in a single operation. Preliminary tests were carried out with a slightly smaller tank, and the correct techniques developed before proceeding with the coating operations on the tank truck.

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KEL-F Dispersions are finely divided fluorocarbon plastic solids in a volatile medium. Applied by spray, dip or spread coating, they are fused by heat into a tough, impervious coating—firmly bonded to the surface on which applied, and providing a chemical and temperature resistant surface that is anti-sticking and self-cleaning.

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